ORGANOMETALLICS

Synthesis and Reactions of a Cyclopentadienyl-Amidinate Titanium *tert*-Butoxyimido Compound

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Supporting Information

ABSTRACT: We report the first detailed reactivity study of a group 4 alkoxyimido complex, namely $Cp^*Ti\{PhC(N^iPr)_2\}$ -(NO^tBu) (19), with heterocumulenes, aldehydes, ketones, organic nitriles, $Ar^{F_3}CCH$, and $B(Ar^{F_3})_3$ ($Ar^{F_5} = C_6F_5$). Compound 19 was synthesized via imide/alkoxyamine exchange from $Cp^*Ti\{PhC(N^iPr)_2\}(N^tBu)$ and ^tBuONH₂.



Reaction of 19 with CS₂ and Ar'NCO (Ar' = 2,6-C₆H₃ⁱPr₂) gave the [2 + 2] cycloaddition products Cp*Ti{PhC(NⁱPr)₂}-{SC(S)N(O'Bu)} and Cp*Ti{PhC(NⁱPr)₂}{N(O'Bu)C(NAr')O}, respectively, whereas reaction with 2 equiv of TolNCO afforded Cp*Ti{PhC(NⁱPr)₂}{OC(NTol)N(Tol)C(NO'Bu)O} following a sequence of cycloaddition-extrusion and cyclo-addition-insertion steps. Net NO'Bu group transfer was observed with both 'BuNCO and PhC(O)R, yielding the oxo-bridged dimer [Cp*Ti{PhC(NⁱPr)₂}(μ -O)]₂ and either the alkoxycarbodiimide 'BuNCNO'Bu or the oxime ethers PhC(NO'Bu)R (R = H (25a), Me (25b), Ph (25c)). DFT studies showed that in the reaction with PhC(O)R (R = H, Me) the product distribution between the *syn* and *anti* isomers of PhC(NO'Bu)R was under kinetic control. Reaction of 19 with ArCN gave the Ti=N_a insertion products Cp*Ti{PhC(NⁱPr)₂}{NC(Ar)NO'Bu} (Ar = Ph (28), 2,6-C₆H₃F₂ (27), Ar^{F₅} (26)) containing *tert*-butoxybenzimidamide ligands. Reaction of 19 or 26 with an excess of Ar^{F₅}CN across the Ti=N_a bond of 26. Reductive N_a-O_β bond cleavage was observed with Ar^{F₅}CCH, forming Cp*Ti(O'Bu){NC(Ar^{F₅})C(H)N(ⁱPr)C(Ph)N(ⁱPr)} (30). Addition of 2 equiv of [Et₃NH][BPh₄] to 19 in THF-d₈ resulted in protonolysis of the amidinate ligand, forming [PhC(NHⁱPr)₂]{BPh₄] and the cationic alkoxyimido complex [Cp*Ti{NO'Bu}(THF-d₈)₂]⁺. In contrast, reaction with B(Ar^{F₅})₃ resulted in elimination of isobutene and formation of Cp*Ti{PhC(NⁱPr)₂}{ η^2 -ON(H)B(Ar^{F₅})₃}.

INTRODUCTION

Group 4 alkyl- and arylimido complexes (L)M=NR (M = group 4 metal, R = alkyl, aryl) have been studied in considerable depth over the past 20 years.¹ Much of this work has centered on the wide range of stoichiometric reactions that the polar M=N multiple bond (formally a $\sigma^2 \pi^4$ triple bond in most instances^{1e,2,3}) undergoes with both saturated and unsaturated substrates. Catalytic applications of these complexes usually involve the imido group as the reactive site, most notably in alkene, allene, and alkyne hydroamination.⁴ In some instances it acts as a supporting or spectator ligand, in particular in the context of olefin polymerization for the group 4 metals.⁵ Alongside this chemistry, and building on initial reports by Wiberg⁶ and Bergman, the related terminal dialkyl- or diarylhydrazido(2-)complexes $(L)M = N - NR_2$ (R = alkyl, aryl) have increasingly been studied in terms of synthesis and reactivity for $M = Ti_{1}^{8}$ Zr⁹ in particular. Terminal alkylidene hydrazido complexes of titanium, (L)Ti=NNCRR' (R, R' = hydrocarbyl, H)—which can alternatively be viewed as highly reduced diazoalkane species-have also been reported and studied for their reactions with H₂, silanes, and unsaturated polar and nonpolar substrates.¹⁰ Investigations of the bonding in group 4 dialkyl-,

diaryl- and alkylidenehydrazido complexes have accompanied the synthetic, structural, and reactivity studies.^{8e,g,k,s,9b,11} Like their imido analogues, group 4 hydrazido complexes undergo a range of reactions at the M=N_a bond, undergoing cyclo-addition, cycloaddition–insertion, cycloaddition–elimination, and NNR₂ group transfer with unsaturated substrate-s,^{8a,f,h,l-n,p-r,u,y,9f,h} and also 1,2-addition of Si–H or Si–Cl bonds.^{8t,w} In addition, both N_a–N_β bond reductive cleavage and insertion reactions with oxidizable substrates such as CO,⁷ isonitriles,^{8r,9a} and alkynes^{8h,p,9m,12} are also becoming established for these complexes (in contrast to the situation for their group 5 or 6 analogues, which show no such reactivity with unsaturated substrates¹³).

Prompted by this unusual and interesting chemistry, we have very recently started to develop synthetic methodologies for the hitherto unknown titanium alkoxyimido complexes (L)Ti= NOR,¹⁴ with the hope of accessing both new Ti= N_{α} multiplebond chemistry as well as N_{α} – O_{β} bond reactivity. For example, the mechanism^{8p,9i,m} of alkyne insertion into the N_{α} – N_{β} bond of certain titanium and zirconium hydrazides is related to that

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Organometallics



Figure 1. Selected examples of previous transition-metal alkoxyimido complexes.^{14,16}

for (reductive) cleavage of the peroxide ligand $O_{\alpha}-O_{\beta}$ bond in $Cp*_{2}Hf(R)(OO^{t}Bu)$ to form $Cp*_{2}Hf(OR)(O^{t}Bu)$ (R = H, alkyl).¹⁵ However, although transition-metal imido and hydrazido compounds have been extensively studied across the transition-metal series, the corresponding alkoxyimides remain poorly explored, in terms of both synthesis and bonding and also with respect to the reactivity of such complexes.

The first alkoxyimido complex was reported in the early 1980s, namely the trimetallic ruthenium structure $\operatorname{Ru}_3(\operatorname{CO})_{10}(\operatorname{NOMe})$ (1; Figure 1),^{16a} followed a few years later by the monomeric Ta(NOMe)Cl₃(bipy) (2)^{16b} and half-sandwich group 5 (e.g., 3) and 6 complexes.^{16b,c,17} We recently reported the syntheses and electronic structures of the first group 4 alkoxyimido complexes (e.g., 4–6) along with a preliminary example of their reactivity with alkynes (vide infra).¹⁴ Rational synthetic routes to terminal alkoxyimido complexes have so far included methylation of metal nitroso compounds,^{16a,18} dehydrohalogenation of metal amide compounds.¹⁴ Crystallographic studies and DFT calculations suggest that, like hydrazides and imides, the alkoxyimido ligand is a four-electron donor with a formal charge of 2–, capable of bonding to transition metals through one σ - and two π -bonds.¹⁴

To date, the reactivity of alkoxyimido complexes is very limited. Reactions of 1 with certain alkynes formed Ru₃(CO)₉(μ_3 -NOMe)(μ_3 - η^2 -RCCPh) (R = H, Ph),¹⁹ while heating at 90 °C in toluene resulted in N–O bond cleavage to give the corresponding nitrene Ru₃(CO)₉(OMe)(N).²⁰ Hydrogenation of 1 in the presence of Ru₃(CO)₁₂ generated a mixture of species, including Ru₅(μ -H)₃(CO)₁₃(μ_4 -NH)(μ_3 -OMe), also following reductive N–O bond cleavage.²⁰ Furthermore, transmetalation of 1 using CpMo(CO)₃H led to the mixed Ru/Mo trimetallic structures Ru₂Mo(μ -H)-(CO)₈(Cp)(μ_3 -NOMe) and Ru₂Mo(μ -H)(CO)₈(Cp)(μ_3 -NH).^{17c}

Reaction of $Ti(NO^{t}Bu)Cl_{2}(NHMe_{2})_{2}$ or $Ti(NO^{t}Bu)-Cl_{2}(py)_{3}$ (4; Figure 1) with neutral tridentate or lithiated anionic nitrogen based ligand sets yielded a range of group 4 alkoxyimido complexes: for instance, $Ti(NO^{t}Bu)(Me_{3}[9]-aneN_{3})Cl_{2}$ (5, $Me_{3}[9]aneN_{3}$ = trimethyl-1,4,7-triazacyclononane; Figure 1) and $Ti(N_{2}N^{Me})(NO^{t}Bu)(py)$ (6, $N_{2}N^{Me}$ = $MeN(CH_{2}CH_{2}NSiMe_{3})_{2}$; Figure 1).¹⁴ However, as yet only

one reaction involving a titanium alkoxyimide ligand has been reported, namely the reaction of PhCCMe and **6** resulting in 7 (Figure 2) via reductive cleavage of the N_{α} -O_{β} bond and



Figure 2. Reaction products following reaction of $Ti(N_2N^{Me})(NX)$ -(py) (X = O^tBu (6), NPh₂ (8)) with PhCCMe.^{8h,p,14a} The fragments derived from the Ti=NX and alkyne moieties are shown in red and blue, respectively.

formation of two new N–C bonds.^{14a} The mechanism proceeds via initial cycloaddition of the alkyne to $Ti=N_{\alpha}$ followed by $N_{\alpha}-O_{\beta}$ bond cleavage and net insertion into one of the N–SiMe₃ bonds of the N₂N^{Me} ligand. In contrast, the corresponding reaction of PhCCMe with the hydrazide analogue $Ti(N_2N^{Me})(NNPh_2)(py)$ (8) also gives initial Ti=N cycloaddition but ultimately yields the vinylimido product $Ti(N_2N^{Me})\{NC(Ph)C(Me)NPh_2\}(py)$ (9; Figure 2).^{8h,p}

To develop further the chemistry of titanium alkoxyimido systems, we turned to the cyclopentadienyl-amidinate supporting ligand set which, together with related ligands,^{8m,n,x,21} has proved a robust and flexible platform for studying and comparing the reactivity of imido and also dimethyl-, diphenyl-, and alkylidenehydrazido compounds of the type Cp*Ti{MeC-(NⁱPr)₂}(N^tBu) (10), Cp*Ti{MeC(NⁱPr)₂}(NAr) (Ar = Tol (11a), Xyl (11b, Xyl = 2,6-C₆H₃Me₂)),²² Cp*Ti{MeC-(NⁱPr)₂}(NNR₂) (R = Ph (12), Me (13)),^{8h,q,t,u,w} and Cp*Ti{MeC(NⁱPr)₂}(NNCPh₂) (14).^{10f} In this contribution we report the first imide/alkoxyamine exchange strategy for the synthesis of a terminal alkoxyimido complex and report on its reactivity with unsaturated molecules, including CS₂, isocyanates, aldehydes, ketones, nitriles, Ar^{Fs}CCH, and B(Ar^{Fs})₃.

RESULTS AND DISCUSSION

Synthesis and Bonding Analysis of Cyclopentadienyl-Amidinate Alkoxyimido Compounds. In our previous report we found that stable monomeric titanium alkoxyimido compounds were only accessible using the bulky *tert*-butoxy group. Therefore, in this present study, we have focused exclusively on this substituent.^{14b} We have previously shown that all of the complexes $Cp^*Ti\{MeC(N^iPr)_2\}(NAr)$ (11),^{22d} $Cp^*Ti\{MeC(N^iPr)_2\}(NNR_2)$ (R = Ph (12), Me (13))^{8u} and $Cp^*Ti\{MeC(N^iPr)_2\}(NNCPh_2)$ (14)^{10f} can be synthesized from the readily prepared^{22d} $Cp^*Ti\{MeC(N^iPr)_2\}(N^tBu)$ (10) via *tert*-butylimide-arylamine/hydrazine exchange reactions. Consequently, this strategy was also employed to make the corresponding alkoxyimido complex $Cp^*Ti\{MeC(N^iPr)_2\}$ (NO'Bu) (15) from 10 and ^tBuONH₂, itself conveniently prepared in multigram quantitites.²³ Compound 15 was isolated as a dark green viscous oil in effectively quantitative yield (eq 1).



Although 15 could be obtained in analytically pure form, difficulty in handling prompted us to develop a more crystalline derivative. Alternative amidinate ligand precursors, Li[PhC-(NⁱPr)₂] (16),²⁴ Li[MeC(NTol)₂],²⁵ and Li[^tBuC(NⁱPr)₂],²⁵ were prepared by nucleophilic addition to the corresponding carbodiimide and subsequently reacted with Cp*Ti(NtBu)Cl-(py) $(17)^{26}$ by analogy with the synthesis of 10^{22d} and certain analogues.^{22c,d} The reactions with Li[MeC(NTol)₂] and Li[^tBuC(NⁱPr)₂] proved unsuccessful, the latter being consistent with previous results regarding the synthesis of aluminum amidinate complexes, where steric constraints prevented ligand complexation.²⁵ However, in the case of 16, heating at 60 °C for 18 h in benzene afforded Cp*Ti{PhC- $(N^{i}Pr)_{2}$ (N^tBu) (18; Scheme 1) as a dark red oil in nearquantitative yield. Subsequent tert-butylimide/tert-butoxyamine exchange between 18 and 'BuONH2 yielded Cp*Ti{PhC-(NⁱPr)₂}(NO^tBu) (19; Scheme 1), again in quantitative yield when followed by ¹H NMR spectroscopy. Larger scale reactions afforded 19 as a fine green powder in multigram quantities and 70% isolated yield. This is the first example of an alkoxyimide

synthesis utilizing an alkylimide/alkoxyamine ligand exchange methodology.

The molecular structure of **19**, determined by X-ray crystallography, is shown in Figure 3 and selected bond lengths



Figure 3. Displacement ellipsoid plot (20% probability) of Cp*Ti- ${PhC(N^{i}Pr)_{2}}(NO^{t}Bu)$ (19). H atoms are omitted for clarity.

and angles are given in Table 1. Compound 19 possesses a three-legged piano-stool geometry around titanium with η^5 - C_5Me_5 , $\kappa^2 N_1N'$ -PhC(NⁱPr)₂, and η^1 -NO^tBu ligands. The bond lengths and angles associated with the $Cp*Ti{PhC(N^{i}Pr)_{2}}$ fragment are similar to those found for the xylylimido and hydrazido homologues $11b_{,}^{22d}$ 12, $13,^{8u}$ and 14^{10f} and for cyclopentadienyl and amidinate complexes of titanium(4+) in general.²⁷ The metric parameters associated with the Ti= NO^tBu group are similar to those for the previously reported titanium *tert*-butoxyimides.¹⁴ The short average Ti(1)-N(1)distance of 1.713(2) Å lies within the expected range for titanium tert-butoxyimides (range 1.686(2)-1.734(2) Å) and, together with the near-linear Ti=N-O average angle of 162.9(2)°, indicates substantial Ti= N_{α} multiple-bond character as expected. The Ti(1)-N(1) bond distance is comparable within error to that of the dimethylhydrazide 13 (1.723(2) Å)but significantly shorter than for the xylylimido and diphenyland alkylidenehydrazido compounds 11b, 12, and 14 (1.738(2), 1.734(2), and 1.751(2) Å, respectively). The average N(1)-O(1) bond distance (1.379(3) Å) is indicative of a single bond,²⁸ and the average N(1)-O(1)-C(1) angle of 112.8(2)° is consistent with the bent geometry found for (L)M=N-OR linkages in general.²⁷ In our previous studies¹⁴ of tertbutoxyimido compounds we found that the $Ti=N_{\alpha}$ distances were generally intermediate between those in the homologous alkylimido and phenylimido analogues and shorter than in the diphenylhydrazido counterparts. Although a crystallographically characterized alkylimido analogue is not available for

Scheme 1. Synthesis of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19) Starting from Li[PhC(NⁱPr)₂] (16) and Cp*Ti(N^tBu)Cl(py) (17)



	Ti(1)–Cp _{cent}	2.054 [2.048]	Ti(1)-N(3)	2.121(3) [2.119(3)]
	Ti(1)-N(1)	1.709(3) [1.716(3)]	N(1) - O(1)	1.381(4) [1.377(4)]
	Ti(1)-N(2)	2.114(3) [2.131(3)]	O(1)-C(1)	1.460(5) [1.456(5)]
	Cp_{cent} - $Ti(1)$ - $N(1)$	122.02 [120.97]	N(2)-Ti(1)-N(3)	64.02(12) [63.99(12)]
	Cp_{cent} -Ti(1)-N(2)	122.46 [122.26]	Ti(1)-N(1)-O(2)	163.8(3) [161.9(3)]
	Cp_{cent} -Ti(1)-N(3)	120.85 [120.95]	N(1) - O(1) - C(1)	113.1(3) [112.4(3)]
¹ Cp _{cent} is the computed centroid for the Cp* ring carbons. Values in brackets are for the other crystallographically independent molecule.				

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Cp*Ti{PhC(N^iPr)_2}(NO^tBu)$ (19)^{*a*}

comparison, the experimental data for 19 in comparison with 11b, 12, 13, and 14 appear consistent with these trends.

A number of computational studies into the bonding of group 4 imido and hydrazido complexes have previously been carried out, and the electronic structure of the M==NR and M==NNR₂ (R = alkyl, aryl) moieties is well understood.^{2,8e,g,k,s,9b,11} So far, however, there has been only one computational study of any alkoxyimido complex. This focused on the model compound Ti(NOMe)Cl₂(NHMe₂)₂ (an analogue of the real compound possessing a Ti==NO^tBu group), in comparison with the imido and hydrazido systems Ti(NR)Cl₂(NHMe₂)₂ (R = Me, Ph, NMe₂).^{14b} To gain further understanding into the bonding of alkoxyimido complexes, DFT calculations were carried out on the model system CpTi{MeC(NMe)₂}(NOMe) (**10_OMe**) using the B3PW91 functional. The geometry, key orbital representations, and associated energies are shown in Figure 4. Comparative DFT



Figure 4. (top) DFT model compound CpTi{MeC(NMe)₂}(NOMe) (1Q_OMe) and associated isosurfaces and energies of the HOMO (π_v) and HOMO-2 (π_h). (bottom) DFT computed isodesmic reaction between 1Q_Me and MeONH₂ (electronic energy).

calculations have previously been carried out on the imido and hydrazido homologues CpTi{MeC(NMe)₂}(NR) (R = Me (**1Q_Me**), Ph (**1Q_Ph**), NMe₂ (**1Q_NMe**₂, pyramidal N_β), NPh₂ (**1Q_NPh**₂, planar N_β)).^{8u} Additional details for these model complexes can be found in the Supporting Information (Figure S1a,b). The DFT calculations predict Ti=NR bond lengths in the order Ti=NMe (1.688 Å) < Ti=NOMe (1.698 Å) < Ti=NOMe (1.698 Å) < Ti=NNMe₂ (1.705 Å) < Ti=NPh (1.709 Å) < Ti=NNPh₂ (1.713 Å), consistent with the experimental and previous computational results described above.^{14b}

All of the complexes have formal $Ti \equiv N_{\alpha}$ triple bonds containing two orthogonal $3d_{\pi}-2p_{\pi}$ interactions (denoted π_{v} and π_{h}) with a predominantly ligand-based, out-of-phase 2p AO combination from the nitrogen atoms of the amidinate ligand being either the HOMO-1 or HOMO (for **10_Me**). This latter MO can mix with π_{h} under the approximate C_{s} symmetry of CpTi{MeC(NMe)₂}(NR). Because of this mixing effect and the orientation of the -Ph,-NMe2, and -NPh2 substituents (vide infra), the energy of $\pi_{\rm h}$ is relatively insensitive to the N_a substituents and varies nonsystematically between the complexes. However, the energy of π_v is very dependent on the N_{α} substituent. As described previously,⁸^u in the case of the $-NR_2$ groups (1Q_NMe₂ and 1Q_NPh₂) the N_{β} lone pair (LP) destabilizes π_{v} through an antibonding interaction (the energy of π_v in these complexes is -4.30 and -4.24 eV, respectively; cf. -5.47 eV in the benchmark model 1Q Me). Likewise, in **1Q** Ph, interaction of one of the filled –Ph ring π -MOs with π_v is also destabilizing (energy of π_v –4.98 eV). As can be seen in Figure 4, the -OMe substituent of 1Q OMe possesses an approximately pure 2p lone pair due to the formal sp² hybridization at O. This LP is oriented (dihedral angle Cp_{cent} -Ti···O-R = 130.0° in 1Q OMe; cf. 125.2° in the real compound 19) such that it can interact, in an antibonding way, with both $\pi_{\rm h}$ and $\pi_{\rm v}$ which results in a $\pi_{\rm v}$ energy of -4.92 eV. The destabilizing effect is thus comparable to that found in 1Q Ph but less than that in the hydrazido analogues 1Q NR₂. This trend is analogous to that found in the model compounds $Ti(NR)Cl_2(NHMe_2)_2$ (R = OMe, Me, Ph, NMe₂).^{14b}

The trends in experimental and computed Ti=NR bond distances can also be accounted for by the nature of the R substituent. As noted previously,^{8u} a second-order NBO (natural bond orbital) perturbation analysis²⁹ of 1Q_NR, (R = Me (pyramidal N_{β}), Ph (planar N_{β})) found significant donation (19.2 and 26.1 kcal mol⁻¹, respectively) from the $-NR_2$ LP into the Ti= $N_{\alpha} \pi^*_{\nu}$ NBO, thus lengthening the Ti= N_{α} bond. In the case of 1Q Ph a smaller interaction between a filled ring π orbital and π^*_v (12.1 kcal mol⁻¹) was accompanied by competition from a Ph ring π^* acceptor orbital for the -NPh 2p AO (as indicated by a stabilization energy of 26.2 kcal mol⁻¹ between π_v and a Ph ring π^* NBO). This combination of "push-pull" effects accounts for the longer M=NR bonds found in general for arylimido compounds in comparison to their alkylimido counterparts.^{27,30} In 1Q OMe the NBO analysis found donation from the oxygen LP into both π^*_{v} and π^*_{h} (interaction energy 8.7 and 9.7 kcal mol⁻¹, respectively) as a consequence of the orientation of the –OMe group. The net interaction energy of 18.4 kcal mol^{-1} is comparable to that for 1Q NMe₂ for the Ti=N_a π^* orbital alone and consistent with the experimental and computational similarity of the (L)Ti=NOR and (L)Ti=NNMe₂ bond distances and the lengthening of the (L)Ti=NOR bond in comparison to (L)Ti=NR ($R = {}^{t}Bu$ or Me) in both cases.

Figure 4 also shows the DFT computed reaction of 1Q_Me and MeONH₂, forming 1Q_OMe and MeNH₂. The ΔE value of -3.9 kcal mol⁻¹ is comparable to those for the corresponding processes for PhNH₂, Ph₂NNH₂, and Me₂NNH₂ ($\Delta E = -2.5, -5.1, -4.0$ kcal mol⁻¹, respectively),^{8u} consistent with experiment where the *tert*-butylimido/amine or hydrazine exchange reactions of Cp*Ti{RC(NⁱPr)₂}(N^tBu) (R = Me (10), Ph (18)) are all quantitative.

Reactions with Heterocumulenes. As mentioned, the reaction chemistry of alkoxyimido compounds in general is virtually unexplored and so we have started to develop their reactions with a range of unsaturated substrates. Group 4 imido and hydrazido complexes typically undergo [2 + 2] cycloaddition reactions with heterocumulenes such as CO_2 , isocyanates, and their heavier congeners. Further reactions such as retrocyclization, extrusion of a new organic species, and insertion of a second molecule of substrate into the first-formed metallacycles have all been observed. $^{1a-f,8a,f,h,l-n,p-r,u,v,9f,h}$ The most relevant systems for comparison with 19 are clearly the homologous cyclopentadienyl-amidinate systems $Cp^*Ti\{MeC(N^iPr)_2\}(NR)$ (R = 'Bu (10), aryl (11), NPh₂ (12), NMe₂ (13), NCPh₂ (14)) which have been studied in considerable detail previously. ^{8h,q,t,u,w,10f,22}

When the reaction of **19** with CO_2 (ca. 1.1 atm pressure) was followed by ¹H NMR spectroscopy in C_6D_6 at room temperature, mixtures from which no single products could be identified were observed. In contrast, addition of 1 equiv or more of CS_2 to a benzene solution of **19** resulted in the single apparently C_s -symmetric product **20** according to ¹H NMR spectroscopy at room temperature. However, on cooling a sample to -60 °C in toluene- d_8 the PhC(NⁱPr)₂ ligand isopropyl resonances decoalesced into four doublets (diastereotopic CHM e_2) and two septets (CHM e_2), consistent with the C_1 -symmetric thiocarbamate-type [2 + 2] cycloaddition product Cp*Ti{PhC(NⁱPr)₂}{SC(S)N(O^tBu)} (**20**; eq 2).



The ¹³C NMR spectrum at -50 °C revealed an SCS resonance at δ 148.1 ppm, analogous to the hydrazido cycloaddition

products Cp*Ti{MeC(NⁱPr)₂}{N(R)C(S)S} (R = NMe₂, NPh₂, NNCPh₂; ca. δ 150–160 ppm).^{8u,10f} Compound **20** was isolated in 65% yield and characterized by elemental analysis and ¹H and ¹³C NMR and IR spectroscopy. No further reaction with CS₂ was observed at room temperature. Like the hydrazide-derived products, **20** is stable in solution for days, although heating at 70 °C for up to 1 week generated unknown mixtures. This is in contrast to the arylimido counterparts Cp*Ti{MeC(NⁱPr)₂}{N(Ar)C(S)S} (Ar = Xyl, Tol) which extrude the corresponding isothiocyanate, ArNCS, forming the sulfido-bridged dimer [Cp*Ti{MeC(NⁱPr)₂}(μ -S)]₂.^{22d}

The reactions of **19** with the representative isocyanates Ar'NCO, TolNCO, and ^tBuNCO (Ar' = $2,6-C_6H_3^{i}Pr_2$) are summarized in Scheme 2 and discussed below. No reaction was observed between **19** and the isothiocyanate Ar'NCS at room temperature, while heating at 60 °C gave complex mixtures. Reaction with TolNCS (1 or 2 equiv) also resulted in unknown mixtures, and so reactions with isothiocyanates were not pursued further.

Reaction with the bulkier Ar'NCO formed the cycloaddition product Cp*Ti{PhC(NⁱPr)₂}{OC(NAr')N(O^tBu)} (21) within 90 min at room temperature. The compound was isolated in 40% yield, and no further reaction was observed. Although 21 could not be structurally authenticated, the ¹H NMR spectrum of 21 in toluene- d_8 at -30 °C is indicative of C_1 symmetry and a ROESY NMR experiment was consistent with the $\kappa^2 N$,Ocoordination mode shown in Scheme 2. The IR spectrum shows a ν (C=N) band at 1631 cm⁻¹, which compares well with a number of imido- and hydrazido-derived analogues of the type Cp*Ti{MeC(NⁱPr)₂}{N(R)C(NAr')O} (R = aryl, NPh₂, NCPh₂) (ν (C=N) in the range 1609–1622 cm⁻¹).^{8u,10f,22d} Like these previous arylimido and hydrazido products, 21 was stable to carbodiimide (Ar'NCNO^tBu) elimination, although unknown decomposition species were observed by ¹H NMR spectroscopy over 2 days in C₆D₆.

When it was followed on the NMR tube scale, the reaction between **19** and 1 equiv of TolNCO gave unknown mixtures. However, upon reaction with 2 equiv of TolNCO, one major





 $^{a}\text{Ar}' = 2,6 \cdot \text{C}_{6}\text{H}_{3}^{\text{i}}\text{Pr}_{2}.$

product (22) was formed within 30 min, which was isolated in 60% yield on scale-up. Compound 22 was identified by NMR spectroscopy and X-ray crystallography as the "double-insertion" compound $Cp*Ti{PhC(N^{2}P_{2})}{OC(NTol)N(Tol)-C(NO^{t}Bu)O}$. The solid-state structure is shown in Figure 5,



Figure 5. Displacement ellipsoid plot (20% probability) of Cp*Ti- ${PhC(N^{i}Pr)_{2}}{OC(NTol)N(Tol)C(NO^{i}Bu)O}$ (22). H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{Ti}(PhC(N^{i}Pr)_{2})OC(NTol)N(Tol)C(NO^{Tbu})O$ (22)^{*a*}

Ti-Cp _{cent}	2.049	N(4) - C(5)	1.4141(16)	
Ti(1)-N(2)	2.0726(10)	N(4) - C(6)	1.4024(15)	
Ti(1) - N(3)	2.0979(10)	N(4) - C(7)	1.4267(16)	
Ti(1) - O(2)	1.9197(9)	N(5) - C(6)	1.2822(17)	
Ti(1) - O(3)	1.9527(9)	O(1) - C(1)	1.4539(15)	
N(1)-C(5)	1.2851(17)	O(2) - C(5)	1.3337(15)	
N(1) - O(1)	1.4242(14)	O(3) - C(6)	1.3184(15)	
Cp_{cent} -Ti(1)-N(2)	114.88	O(2) - Ti(1) - O(3)	84.63(4)	
Cp_{cent} -Ti(1)-N(3)	116.67	O(2) - C(5) - N(4)	115.65(10)	
Cp_{cent} - $Ti(1)$ - $O(2)$	110.36	C(5)-N(1)-O(1)	109.93(10)	
Cp_{cent} - $Ti(1)$ - $O(3)$	113.45	N(1)-O(1)-C(1)	110.71(9)	
N(2)-Ti(1)-N(3)	63.73(4)	C(5)-N(4)-C(6)	117.85(10)	
Ti(1)-O(2)-C(5)	113.21(7)	N(4)-C(6)-O(3)	113.47(10)	
Ti(1)-O(3)-C(6)	131.78(8)	N(4)-C(6)-N(5)	119.30(11)	
Cp_{cent} is the computed centroid for the Cp^* ring carbons.				

and selected bond length and angles are given in Table 2. The solution ¹H and ¹³C NMR spectra are consistent with the solid-state structure, in particular confirming the C_1 symmetry of the compound and the presence of two inequivalent tolyl groups derived from the TolNCO.

The molecular structure shows a five-coordinate titanium center in a four-legged piano-stool geometry. In addition to the η^{5} -C₅Me₅ and $\kappa^{2}N,N'$ -PhC(NⁱPr)₂ supporting ligands, two new Ti–O bonds make up part of the newly formed six-membered ring derived from the two TolNCO moieties and the original NO^tBu fragment of 19. The N(4)–C(5), N(4)–C(6), and N(4)–C(7) bonds are consistent with C–N single bonds, whereas the N(1)–C(5) and N(5)–C(6) bonds are significantly shorter, consistent with the double-bond representation shown in Scheme 2. The structure is reminiscent of the

previously reported Cp*Ti{MeC(NⁱPr)₂}{OC(NR)N(Tol)C-(NTol)O} ($R = NMe_2$, NCPh₂), formed by reaction of 13 or 14 with 2 equiv of TolNCO,^{8u,10f} although in 22 the sixmembered ring has a significantly more nonplanar arrangement. The IR spectrum of 22 shows two ν (C=N) bands at 1623 and 1587 cm⁻¹ which are comparable to those seen in the previous cases (1623, 1604 and 1619, 1599 cm⁻¹ for 13 and 14, respectively). Although the unsymmetrical structure found for 22 has the aforementioned precedents in the hydrazide literature, this type of "double insertion" product is relatively unusual, with C_s -symmetric products of the type Cp*Ti{MeC- $(N^{i}Pr)_{2}$ {OC(E)N(R)C(E)O} (R = Tol, NPh₂; E = O, NTol) usually being formed in the case of reactions of CO2 or TolNCO with $Cp*Ti{MeC(N^{i}Pr)_{2}}(NR)$ (R = Tol (11a), NPh_2 (12, for CO_2 only)), and these reactions have been studied in detail both experimentally and computationally.^{8u,22a,d,e}

Scheme 3 shows the proposed mechanism for formation of 22, which is analogous to that determined by DFT calculations for 13 and consistent with the reactions of 19 with Ar'NCO and ^tBuNCO (vide infra).^{8u} Thus, [2 + 2] cycloaddition of TolNCO to 19 forms the intermediate 22 int1, which is the analogue of the fully characterized 21. The species 22 int1 is not observed and undergoes extrusion (retrocyclization) of the tert-butoxy carbodiimide 'BuONCNTol, forming the transient titanium oxo species $Cp^{*}Ti{PhC(N^{i}Pr)_{2}}(O)$. Although such species can easily dimerize, they are also able to undergo cycloaddition reactions with carbodiimides or other unsaturated species.^{8a,31} In this case, cycloaddition of the extruded ^tBuONCNTol to the transient oxo species is rapid in comparison with dimerization, either re-forming 22 int1 or the isomeric 22_int2 containing a Ti-N(Tol) single bond. As we have shown previously^{22d} such ureato species are able to insert isocyanates, in this case forming 22. Interestingly, although Scheme 3 proposes 22 int1 as a likely intermediate, this compound apparently does not undergo insertion of TolNCO into the Ti-N(O'Bu) bond in preference to rearrangement to 22 int2. We attribute this to the electronwithdrawing nature of the -O'Bu group decreasing the nucleophilicity of the Ti $-N(O^{t}Bu)$ nitrogen in comparison to Ti-N(Tol) or/and the steric bulk of the *tert*-butyl substituent.

As shown in Scheme 2, reaction of 19 with ^tBuNCO over a period of 16 h resulted in a gradual color change from green to yellow along with formation of a yellow precipitate, identified as the oxo-bridged dimer $[Cp*Ti{PhC(N^{i}Pr)_{2}}(\mu-O)]_{2}$ (23). A number of analogues of 23 have been reported previously from reactions of this type.^{22a,c,d} The molecular structure and selected bond lengths and angles for 23, which lie within the expected ranges,²⁷ are presented in Figure S2 and Table S1 of the Supporting Information. Careful evaporation of the filtrate gave the alkoxycarbodiimide byproduct ^tBuNCNO^tBu (24) as a colorless oil, which was characterized by NMR and IR spectroscopy and high-resolution FI mass spectrometry. The IR spectrum showed ν (C=N) bands at 2257 and 2065 cm⁻¹ in the expected range.³² Unfortunately, due to its relatively high volatility, 24 could only be isolated as a pure sample in ca. 10% yield (sufficient to enable full characterization). However, since the reaction of 19 with ^tBuNCO is quantitative (as judged by ¹H NMR monitoring in C₆D₆ (no intermediates analogous to 21 were observed)), 24 could be isolated as diethyl ether solutions in high yield. No examples of alkoxycarbodiimides have previously been reported, although amino-carbodiimides have been reported previously by others³³ and also by our



Scheme 4. Reaction of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19) with PhC(O)H, PhC(O)Me, and PhC(O)Ph



group via a cycloaddition–elimination protocol similar to that forming 24.^{8u,10f} The cycloaddition–extrusion reaction leading to 23 and 24 is analogous to that found previously for reactions of Cp*Ti{MeC(NⁱPr)₂}(NR) (R = ^tBu (10), Ar (11)) and Cp*Ti{MeC(NⁱPr)₂}(NNMe₂) (13) with ^tBuNCO. With 11 unstable cycloaddition intermediates could be observed, but ultimately in all cases carbodiimides were formed along with the corresponding oxo-bridged dimer.

Reactions with Aldehydes and Ketones. The metathesis reactions between transition-metal imido compounds and organic carbonyls to form ketimines or aldimines via cyclo-addition–elimination reactions is well-established.^{1b,c,e,13b,34} In particular, both Cp*Ti{MeC(NⁱPr)₂}(N^tBu) (10) and Cp*Ti{MeC(NⁱPr)₂}(NTol) (11a) undergo ketone and aldehyde C=O/Ti=NR bond metathesis reactions with MeC(O)Me, PhC(O)Ph, PhC(O)H, and PhCOMe, and in some instances [2 + 2] cycloaddition intermediates were observed.^{22d} By analogy, we reasoned that reactions of 19 with aldehydes or ketones should give access to oxime ethers (i.e., compounds of the general type RC(NOR').³⁵

The main synthetic routes to oxime ethers are reaction of an oxime with carbon electrophiles, such as alkyl halides, epoxides, and activated olefins, and reaction of an aldehyde or ketone with the HCl salt of the alkoxyamine.^{23,35,36} Oxime ethers are

formed as one of two isomers, *syn* or *anti*, where *anti* is defined as a Z arrangement of the nitrogen-bound and highest molecular weight carbon-bound substituents.^{36b} As discussed above, reaction of **19** with ^tBuNCO demonstrated the potential for NO^tBu transfer to another fragment (in that case ^tBuNC, forming ^tBuNCNO^tBu (**24**)). To explore the scope of the NO^tBu group transfer processes further, reactions with selected aldehydes and ketones were carried out. Scheme 4 summarizes the reactions of **19** with PhC(O)H, PhC(O)Me, and PhC(O)Ph, along with the proposed likely intermediates.

Reaction of **19** with PhC(O)H in C₆D₆ at room temperature gave quantitative formation of the oxo-bridged dimer [Cp*Ti-{PhC(NⁱPr)₂}(μ -O)]₂ (**23**) and oxime ether PhC(NOⁱBu)H, (**25a**) in a ca. 4:1 ratio of geometric isomers. Scale-up and distillation (80–110 °C, 8 × 10⁻² mbar) gave **25a** as a colorless oil in 70% yield. On the basis of the ¹H and ¹³C NMR spectra (vide infra), the two isomers are assigned as *anti* (major) and *syn* (minor), denoted **25a**_*anti* and **25a**_*syn* in Scheme 4. Following their formation, no significant interconversion between the two isomers was observed in solution or upon sublimation. This is consistent with previous studies which found that, unlike the case for imines, it is only under harsh thermal or photochemical conditions that *syn*_*anti* isomerization of oxime ethers is observed.³⁷



Figure 6. Gibbs free energy diagram (kcal mol⁻¹) at 298 K for the cycloaddition–extrusion reactions of $Cp*Ti{PhC(N^iPr)_2}(NO^iBu)$ (19) with PhC(O)H (left) and Ph(CO)Me (right). Values in parentheses are the Gibbs free energies at 253 K. The $Cp*Ti{PhC(N^iPr)_2}(O)$ side product is not shown.

Comparison with literature data established the minor isomer as 25a_syn, which gives a diagnostic ¹H NMR singlet for syn-PhC(NO^tBu)H at δ 8.03 ppm.^{36d} Literature data for 25a_anti are more limited, but the presence of the anti-PhC(NO^tBu)H singlet at δ 7.27 ppm is consistent with other NMR studies on the geometric isomerism of oxime ethers.^{36c,38} The $o-C_6H_5$ hydrogens for 25a anti are found at δ 7.85 ppm, consistent with the aryl ring being cis to the O^tBu group.^{36b} The assignments were confirmed by comparison of the experimental ¹³C NMR data with the corresponding ¹³C isotropic magnetic shielding tensors calculated by DFT (Figure S3 of the Supporting Information). Interestingly, the DFT calculations showed that the minor isomer 25a syn is $1.9 \text{ kcal mol}^{-1}$ more thermodynamically stable than 25a anti at 298 K. This suggests that the overall reaction is governed by kinetic/ mechanistic constraints, given that 25a_syn and 25a_anti do not interconvert once formed.

Reaction of **19** with PhC(O)Me at room temperature afforded PhC(NO^tBu)Me^{36e} (**25b**; Scheme 4), which again was readily separated from **23** by distillation in very good yield (75%). The known compound PhC(NO^tBu)Me also exists as a mixture of *syn* and *anti* isomers, **25b**_*syn* and **25b**_*anti*, and the assignments were confirmed by comparison with literature NMR values^{36e} and DFT calculated isotropic ¹³C magnetic shielding tensors. However, in this case it is now the *syn* isomer which is the major species, formed in a ca. 9:1 ratio with respect to the *anti* counterpart. As was also the case for **25a**, DFT calculations found that **25b**_*syn* is more thermodynamically stable than **25b**_*anti* by 5.6 kcal mol⁻¹ at 298 K.

On the basis of DFT studies discussed below, Scheme 4 shows the two likely metallacyclic intermediates, denoted **25_int_R**_{down} and **25_int_R**_{up} (R = H, Me), formed en route to the *anti* and *syn* isomers of **25a** and **25b**, respectively. Metallacycles of this type have been explicitly observed by us previously in the reactions of Cp*Ti{MeC(NⁱPr)₂}(NTol) (11a) with PhC(O)R (R = H, Me, Ph), which ultimately give

the corresponding imines PhC(NTol)R and the μ -oxo dimer $[Cp^*Ti\{MeC(N^iPr)_2\}(\mu\text{-}O)]_2.^{22d}$ The metallacycles 25_in-t_R_up/down differ in the orientation of the substrate-derived R and Ph substituents, each diastereomer leading specifically to one isomer of PhC(NO^tBu)R as illustrated.

Although no intermediates were observed at room temperature in the reactions of 19, when PhC(O)H was added to a precooled toluene- d_8 solution of 19 at -50 °C two products were observed in the ¹H NMR spectrum within 5 min. The spectra were consistent with formation of the cycloaddition intermediates $Cp*Ti{PhC(N^{i}Pr)_{2}}{N(O^{t}Bu)C(Ph)(H)O}$ (25a int), present as major and minor isomers in a ca. 7:3 ratio. Warming to -10 °C gave complete consumption of the minor isomer to form 23 and 25a syn. The major isomer extruded 25a anti only slowly at this temperature, but on warming to 0 °C the reaction reached completion within 30 min. The major and minor isomers are tentatively assigned as the metallacycles $25a_{int}H_{up}$ and $25a_{int}H_{down}$, respectively, but due to the numerous overlapping resonances in the ¹H NMR spectrum it was not possible to assign the data completely. In a similar way, when the reaction of 19 with PhC(O)Me was carried out under analogous conditions, no reaction was observed until -30 °C, and at this point one major cycloaddition intermediate, tentatively assigned as the cycloaddition product $25b_int_Me_{up}$, was observed. This started to undergo extrusion at -10 °C, and upon warming to 0 °C the reaction reached completion within 25 min. Note that although only one cycloaddition intermediate was unambiguously identified at low temperature (because of the low proportion of 19 converting to the other diastereomer), two isomers of the oxime ether (25b syn and 25b anti, 9:1 ratio) were formed on warming, as in the room-temperature experiment.

In an additional attempted crossover-type experiment, PhC(O)H was added to a solution of 19 in toluene- d_8 at -50 °C, at which temperature the cycloaddition products $25a_{int}H_{up}$ and $25a_{int}H_{down}$ were both formed as above

and were stable to extrusion. Subsequently, 1 equiv of TolC(O)H was added and, following a further 10 min at -50 °C, the solution was warmed to room temperature, at which point extrusion took place effectively immediately. The ¹H NMR spectrum showed no detectable consumption of the TolC(O)H, showing that extrusion of PhC(NO^tBu)H from $25a_{int}H_{up}$ and $25a_{int}H_{down}$ is much faster than loss of PhC(O)H to re-form 19 (which could then react with either PhC(O)H or TolC(O)H). For comparison, when the reaction of 19 with TolC(O)H was carried out in a separate NMR tube scale reaction, TolC(NO^tBu)H (25d) was formed immediately as a mixture of anti and syn isomers in a 7:3 ratio, respectively. These were characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectroscopy. In a further NMR tube scale experiment, the reaction of a 1:1 mixture of PhC(O)Hand TolC(O)H with 1 equiv of 19 formed a 1:1 mixture of 25a and 25d, confirming that the two aldehydes can compete effectively when both are available prior to metallacycle formation.

Finally, as mentioned, the tolylimide **11a** reacts with PhC(O)Ph to give the ketimine PhC(NTol)Ph, although this reaction took 9 days to reach completion at room temperature.^{22d} The synthesis of the corresponding oxime ether PhC(NO'Bu)Ph (**25c**) has been previously attempted by Rad and Khalafi-Nezhad et al. during their studies of the use of alcohols and oximes, in the presence of DBU, PPh₃, CCl₄ ,and 'Bu₄NI, to prepare such species.³⁵ We found that addition of PhC(O)Ph to **19** in C₆D₆ quantitatively formed **25c** (Scheme 4), albeit at a much slower rate (2 days at room temperature) than for PhC(O)R (R = H, Me). At 70 °C, the reaction was ca. 90% complete within 2 h and reached quantitative conversion within 17 h. On scale-up, **25c** was isolated by sublimation as a cream-colored solid in 93% yield. The structure was confirmed by X-ray crystallography (Figure S4 and Table S2 of the Supporting Information).

Figure 6 shows the DFT computed reaction profile for the reaction of 19 with PhC(O)R (R = H, Me). The actual experimental molecules have been considered in the calculations. Gibbs free energy values are given at 298 and 253 K, and the calculations include D3 corrections for dispersion (see Computational Details). Two pathways were found, shown in blue (path 1) and red (path 2), leading to anti- and syn-PhC(NO^tBu)R, respectively (R = H, Me). In both cases (\dot{R} = H, Me) the reaction proceeds via an entropically disfavored [2 + 2] cycloaddition of the substrate C=O group to Ti=NO^tBu via TS1, forming the intermediate metallacycle 25 int R_{down} (path 1) or 25_int_R_{up} (path 2). These species differ in the orientation of the R group with respect to the Cp* ligand and are predicted to be observable at low temperature in each case (less unfavorable $T\Delta S$ contribution to the ΔG value for 19 + $PhC(O)R \rightarrow 25_{int}R_{up/down}$; see the ΔG values at 253 K in Figure 6). For R = Me, steric interactions destabilize both metallacycles in comparison with those formed from PhC(O)-H, but 25b_int_Me_{down} is destabilized more (with respect to 25a_int_H_down) than 25b_int_Meup. All of the 25_in $t_{R_{up/down}}$ species are unstable with respect to extrusion of the oxime ether and $Cp^*Ti{PhC(N^iPr)_2}(O)$ (the dimerization energy for this to form 23 was not calculated but is known experimentally to be exergonic).

Two important points should be noted regarding possible extrusion processes from 25_int_R_{up/down}. First, although elimination from 25_int_R_{up/down} of the starting PhC(O)R is predicted to be feasible via transition state TS1 ($\Delta G^{\ddagger} = 17.1$ -

19.7 kcal mol⁻¹), loss of the product PhC(NO^tBu)R is more kinetically favorable (via TS2, $\Delta G^{\ddagger} = 8.6-14.5$ kcal mol⁻¹). Second, elimination of PhC(NO^tBu)R from **25_int_R**_{down} gives exclusively the *anti* isomer, while elimination from **25_int_R**_{up} gives exclusively the *syn* isomer.

The relative energies of TS1, TS2, and **25_int_R**_{up/down} account qualitatively for the experimental observations and product isomer selectivity for R = H, Me. In the case of PhC(O)H, formation of **25a_int_H**_{down} (path 1) via TS1 is kinetically favored by $\Delta\Delta G^{\ddagger} = 2.2$ kcal mol⁻¹. Once formed, extrusion of the thermodynamically less stable product **25a_anti** via TS2 is predicted to be slower than extrusion of **25a_syn** from the minor isomer **25a_int_H**_{up}. In the case of PhC(O)Me, however, the relative energies of TS1 for paths 1 and 2 (and the relative energies of **25b_int_Me**_{up/down} and **25a_int_H**_{up/down}) swap over due to the influence of the substrate –Me group. There is, therefore, a higher kinetic preference for the **25b_int_Me**_{up} metallacycle and, in turn, the more stable product **25b_syn**, in accord with experiment.

Reactions with Nitriles. Although the reactions of nitriles with transition-metal nitrides,³⁹ alkylidenes,⁴⁰ and alkylidynes⁴¹ are very well established, the corresponding reactions with transition-metal imides are almost unknown. The first example was for $Ti(N_2N^{py})(N^tBu)(py)$ $(N_2N^{py} = (2-NC_5H_4)CMe$ (CH₂NSiMe₃)₂) with MeCN and gave rise to the dimeric complex $Ti_2(N_2N^{py})_2{\mu-NC(Me)(N^tBu)}_2$.⁴² More recently, reactions of fluorinated benzonitriles $Ar^{F_x}CN$ ($Ar^{F_x} = Ar^{F_2}$ (2,6- $C_6H_3F_2$, $Ar^{F_5}(C_6F_5)$ with diamido-amine- or diamido-ethersupported hydrazides (L)Ti(NNPh₂)(py)_n (L = N_2N^{Me} , N_2N^{py} , $O(CH_2CH_2NSiMe_3)_2$; n = 1, 2) gave net $Ti=N_{\alpha}$ insertion products of the type (L)Ti{NC(Ar^{F_x})NNPh₂}(py)_n containing a new class of hydrazonamide ligand.^{8p,r,12} These reactions are reminiscent of the Zr=P insertion reaction of Cp₂Zr(PMes*)- (PMe_3) (Mes^{*} = 2,4,6-C₆H₂^tBu₃) with PhCN.⁴³ Very recently, we found that the alkylidene hydrazide $Cp^*Ti\{MeC(N^iPr)_2\}$ -(NNCPh₂) (14) undergoes head-to-tail coupling of two molecules of ArCN (Ar = Ph, Ar^{F₅}) across the $Ti=N_{\alpha}$ bond to form $Cp*Ti{MeC(N^{i}Pr)_{2}}{N(NCPh_{2})C(Ar)NC(Ar)N}$, containing a six-membered metallacycle.^{10f} Although hydrazonamide-type intermediates were proposed, none were observed experimentally. In contrast, none of the imido analogues of 14, namely 10 and 11, showed any reactivity toward nitriles. The double nitrile addition reactions of 14 were the first of their kind for any hydrazido or related complex, although multiple coupling of two alkynes⁴⁴ or of an alkyne and a nitrile^{8r} across (L)Ti=NR (R = hydrocarbyl, NPh₂) bonds are known. The only related example of a similar double addition of nitriles was reported for the transient oxo and sulfido complexes Cp*2Zr-(E) (E = O, S).⁴⁵

Scheme 5 shows the reactions of **19** with various benzonitriles ArCN (Ar = Ph, Ar^{F_2} , Ar^{F_5}), varying the extent of fluorination of the phenyl ring. When it was monitored on an NMR tube scale in C_6D_6 , the reaction with $Ar^{F_5}CN$ was complete within 5 min to give $Cp^*Ti\{PhC(N^iPr)_2\}\{NC(Ar^{F_5})-NO^tBu\}$ (**26**), as established by X-ray diffraction (vide infra). The corresponding reaction with $Ar^{F_2}CN$ was slightly slower (80% and 100% conversion to **27** after 5 min and 1 h, respectively), whereas with PhCN the reaction only reached completion, forming **28**, after 19 h (70% after 1 h). The NMR spectra for **26–28** were very similar, consistent with the formation of the new *tert*-butoxybenzimidamide complex $Cp^*Ti\{PhC(N^iPr)_2\}\{NC(Ar)NO^tBu\}$ in each case. Compounds **27** and **26** were isolated on a preparative scale as a

Scheme 5. Reaction of $Cp*Ti{PhC(N^{i}Pr)_{2}}(NO^{t}Bu)$ (19) with Benzonitriles^{*a*}



^aThe inset gives the likely metallacycle intermediate (not observed).

green oil or solid in 97% and 33% yields, respectively, and characterized by ¹H, ¹³C, and ¹⁹F NMR, mass, and IR spectroscopy and elemental analysis. The low yield for **26** is attributed to its high solubility. Attempted scale-up of the reaction with PhCN was unsuccessful, producing unknown mixtures. Similarly disappointing results were obtained using MeCN.

The slower rates of reaction with Ar^{F2}CN and PhCN in comparison with Ar^{F₅}CN are consistent with our previous studies of benzonitriles with $Ti(N_2N^{Me})(NNPh_2)(py)$. DFT calculations showed that increased fluorination of the nitrile substrate both lowered the activation barrier to the intermediate metallacycles Ti(N2NPy){N(NPh2)C(Ar)N} and increased the thermodynamic stability of the final products $Ti(N_2N^{py}){NC(Ar^{F_x})NNPh_2}(py)$ by stabilizing the electronrich Ti=NC(Ar)NPh2 group.^{8r} An analogous intermediate (see inset to Scheme 5) is likely in the reactions reported here (although not observed), and our inability to isolate 28 is attributed to its likely lower stability. To further test these hypotheses, competition experiments were carried out. Reaction of 27 with Ar^{Fs}CN (1 equiv) resulted in immediate formation of 26 and free Ar^{F2}CN, consistent with the more electron deficient nitrile yielding the more thermodynamically stable insertion product. This reaction also highlighted the reversibility of these insertion reactions, which previously had not been observed. Likewise, addition of Ar^{Fs}CN to in situ generated 28 also led to immediate formation of 26 and free PhCN.

Analogues of *tert*-butoxypentafluorobenzimidamide, $H_2NC-(Ar^{F_3})NO^tBu$, such as *O*-alkylbenzamidoximes, $H_2NC-(C_6H_4Br)NOR$, have been shown to be useful in the synthesis of *O*-alkoxyamidine compounds which show antimicrobial activity.⁴⁶ Synthesis of the *O*-alkylbenzamidoxime compounds is nontrivial, requiring multiple steps and toxic stannyl reagents.⁴⁶ With this in mind, ^tBuONH₂ was added to both **26** and **27**, with the hope of effecting benzimidamide/ alkoxyamine exchange and generating **19** and $H_2NC(Ar)$ -

NO^tBu (Ar = Ar^{F₅}, Ar^{F₂}). However, upon addition of ^tBuONH₂ complicated mixtures were observed in the ¹H and ¹⁹F NMR spectra from which no products could be identified.

Diffraction-quality crystals of **26** were grown from a saturated hexane solution at -80 °C. The molecular structure is shown in Figure 7, and selected bond lengths and angles are given in



Figure 7. Displacement ellipsoid plot (20% probability) of Cp*Ti-{PhC(NⁱPr)₂}{NC(Ar^{F₅})NOⁱBu} (26). H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{*}Ti{PhC(N^{i}Pr)_{2}}{NC(Ar^{F_{5}})NO^{t}Bu}$ (26)^{*a*}

Ti-Cp _{cent}	2.046	N(2) - C(1)	1.285(6)
Ti(1) - N(1)	1.747(4)	N(2) - O(1)	1.429(5)
Ti(1) - N(3)	2.080(4)	O(1) - C(8)	1.448(5)
Ti(1) - N(4)	2.074(4)	C(1) - C(2)	1.497(6)
N(1)-C(1)	1.362(5)		
Cp_{cent} - $Ti(1)$ - $N(1)$	121.78	Ti(1)-N(1)-C(1)	167.0(3)
Cp_{cent} -Ti(1)-N(3)	120.38	N(1)-C(1)-N(2)	121.7(4)
Cp_{cent} -Ti(1)-N(4)	121.87	C(1)-N(2)-O(1)	109.5(3)
N(3)-Ti(1)-N(4)	64.97(15)	N(2) - O(1) - C(8)	110.6(3)
Cp_{cent} is the computed centroid for the Cp^* ring carbons.			

Table 3. Compound 26 is a four-coordinate titanium complex with a three-legged piano-stool geometry around the metal and η^5 -C₅Me₅, $\kappa^2 N, N'$ amidinate, and η^1 -tert-butoxypentafluorobenzimidamide ligands. The Ti(1)-N(1) and N(2)-C(1) bond lengths (1.747(4) and 1.285(6) Å, respectively) indicate a multiple Ti=N bond and C=N double bond, whereas the N(1)-C(1) and N(2)-O(1) bond lengths (1.362(5) and 1.429(5) Å, respectively) are more consistent with single bonds, indicating limited delocalization across the Ti= $NC(Ar^{F_5})NO^tBu$ fragment. In comparison to 19 the Ti(1)-N(1) bond is significantly longer (1.747(4) vs 1.713(2) (average) Å) but is still consistent with a $Ti \equiv N_{\alpha}$ triple bond. Related molecular structures of hydrazonamides (L)Ti-{NC(Ar^{F_x})NNPh₂}(py)_n (n = 1, 2) also show longer Ti=N_{α} bond lengths in comparison to the parent hydrazido compounds $(L)Ti(NNPh_2)(py)_n$, which is explained by the fluorinated aryl ring withdrawing electron density away from $N_{\alpha}^{8r,12}$

Addition of 2 equiv of Ar^{F₅}CN to 19 in C₆D₆ afforded an approximately statistical mixture of 26 and a new product, identified by NMR spectroscopy and X-ray crystallography as $Cp*Ti{PhC(N^{i}Pr)_{2}}{NC(Ar^{F_{5}})NC(Ar^{F_{5}})N(C{Ar^{F_{5}}})N(C{Ar^{$ (29; Scheme 5), after 5 h at room temperature. The compounds 26 (and Ar^{Fs}CN) and 29 are in equilibrium, and warming the NMR tube solution to 60 °C favored 26, as expected on the basis of entropic considerations. Addition of 5 equiv of Ar^{F5}CN to 19 led to the sole formation of 29 within 45 min. On scale-up using 5 equiv of $Ar^{F_5}CN$, 29 was isolated as an orange solid in 49% yield. When pure 29 is dissolved in C_6D_6 , an equilibrium mixture of it and 26 and Ar^{F5}CN is formed (26:29 ratio ca. 50:50; $K_{eq} = 1.4 \times 10^{-4} \text{ M}^2$ after 23 h at room temperature). The ¹H NMR spectrum of **29** in toluene- d_8 at -10 °C showed the formation of a C₁-symmetric product with characteristic inequivalent isopropyl groups on the PhC(NⁱPr)₂ ligand. Restricted rotation on the NMR time scale for two of the fluorinated rings resulted in five separate ¹⁹F resonances per ring in the ¹⁹F NMR spectrum, together with three further resonances for the third ring. On the basis of the solid-state structure, the two constrained rings are assigned to those containing C(9) and C(16).

In contrast to the reaction with $Ar^{F_5}CN$, addition of an excess of $Ar^{F_2}CN$ to **19** gave only the insertion product **27**. This difference between $Ar^{F_2}CN$ and $Ar^{F_5}CN$ is reminiscent of the reactions of **14** with PhCN and $Ar^{F_5}CN$ to form $Cp^*Ti\{MeC-(N^iPr)_2\}\{N(NCPh_2)C(Ar)NC(Ar)N\}$. While the product with $Ar = Ar^{F_5}$ was stable in solution at room temperature, that with Ar = Ph was much more labile and on treatment with 2 equiv of $Ar^{F_5}CN$ underwent exchange of one PhCN unit to give a mixed-nitrile metallacycle.^{10f}

Addition of pentane to an Et₂O solution of **29** and Ar^{F₅}CN followed by slow cooling to 4 °C resulted in diffraction-quality orange crystals. The molecular structure is shown in Figure 8,



Figure 8. Displacement ellipsoid plot (20% probability) of Cp*Ti- ${PhC(N^iPr)_2}{NC(Ar^{F_3})NC(Ar^{F_3})N(C{Ar^{F_3}}NO^tBu)}$ (29). H atoms are omitted for clarity.

and selected bond lengths and angles are given in Table 4. Like Cp*Ti{PhC(NⁱPr)₂}{OC(NTol)N(Tol)C(NO^tBu)O} (22), compound 29 is a half-sandwich titanium complex with a four-legged piano-stool geometry around the metal and η^{5} -C₅Me₅ and $\kappa^{2}N,N'$ amidinate ligands. The solid-state structure confirms coupling of a further two molecules of Ar^{Fs}CN across the Ti=N_a bond of 26 in a head-to-tail manner, consistent

Table 4. Selected Bond Lengths	s (Å) and Angles (deg) for
$Cp*Ti{PhC(N^{i}Pr)_{2}}{NC(Ar^{F_{5}})N}$	$NC(Ar^{F_5})N(C(Ar^{F_5})NO^{t}Bu)$
$(29)^{a}$	

Ti(1)-Cp _{cent}	2.089	N(3) - C(8)	1.3634(18)
Ti(1)-N(1)	1.8756(12)	N(3) - C(15)	1.4280(17)
Ti(1) - N(3)	2.1820(11)	N(4) - C(15)	1.2808(18)
Ti(1) - N(5)	2.2267(11)	N(4) - O(1)	1.4058(15)
Ti(1) - N(6)	2.0829(12)	O(1) - C(22)	1.4700(16)
N(1)-C(1)	1.2673(18)	C(1) - C(2)	1.5085(18)
N(2)-C(1)	1.3850(17)	C(8) - C(9)	1.5118(18)
N(2) - C(8)	1.3139(18)		
Cp_{cent} -Ti(1)-N(1)	107.87	Ti(1)-N(1)-C(1)	140.68(10)
Cp_{cent} - $Ti(1)$ - $N(3)$	118.69	C(1)-N(2)-C(8)	117.07(11)
Cp_{cent} -Ti(1)-N(5)	110.92	N(3)-C(15)-N(4)	118.49(12)
Cp_{cent} -Ti(1)-N(6)	120.15	C(15)-N(4)-O(1)	111.19(11)
N(5)-Ti(1)-N(6)	61.60(4)	N(4) - O(1) - C(22)	111.07(10)
N(1)-Ti(1)-N(3)	79.92(5)		

^{*a*}Cp_{cent} is the computed centroid for the Cp* ring carbons.

with the NMR data. Of particular interest is the approximately planar, six-membered metallacycle. The N(1)–C(1) and N(2)–C(1) bond lengths are significantly different (1.2673(18) vs 1.3850(17) Å, $\Delta_{N-C} = 0.118(3)$ Å) and are consistent with N=C and N–C double and single bonds, respectively.²⁸ Although their N(3)–C(8) and N(2)–C(8) counterparts are also different (1.3634(18) vs 1.3139(18) Å) and are consistent with single- and double-bond character, the difference ($\Delta_{N-C} = 0.050(3)$ Å) is somewhat smaller. These data, together with the rather different Ti(1)–N(1) and Ti(1)–N(3) distances ($\Delta_{Ti-N} = 0.306(2)$ Å) suggest (cf. Figure 9) contributions from both A' and A" resonance forms to the



Figure 9. Resonance contributions to the bonding in Cp*Ti{PhC- $(N^iPr)_2$ }{N(C(Ar^{F₅})NO^tBu)C(Ar^{F₅})NC(Ar^{F₅})N} (29). [Ti] = Cp*Ti-{PhC(NⁱPr)_2}.

bonding in 29, leading to the net description A. Likewise, the bond distances to the amidinate ligand, Ti(1)-N(5) and Ti(1)-N(6), are also unequal (2.2267(11) and 2.0829(12) Å, respectively), with the longer Ti(1)-N(5) bond being *trans* to the shorter Ti(1)-N(1) bond. With specific reference to the $NC(Ar^{F_5})NO^tBu$ fragment that remains intact during the reaction, the N(3)-C(15) bond distance is significantly longer than that found in **26** (1.4280(17) vs 1.362(5) Å, respectively), which is attributed to the change in nitrogen hybridization from sp in 26 to sp² in 29 and a loss of conjugation between N(3)and C(15). Otherwise, the other geometric parameters are similar to those seen in 26. The structural parameters for the six-membered metallacycle in 29 are similar to those in the corresponding fragment of Cp*Ti{MeC(NⁱPr)₂}{N(NCPh₂)- $C(Ar^{F_5})NC(Ar^{F_5})N$, except in that case the contribution from the resonance form corresponding to A'' in Figure 9 seemed to be slightly larger ($\Delta_{\rm N-C}$ = 0.080(7) and 0.014(7) Å in comparison with the values mentioned above) while the Scheme 6. Potential Pathways for the Formation of $Cp*Ti{PhC(N^iPr)_2}{N(C(Ar^{F_5})NO^tBu)C(Ar^{F_5})N(Ar^{F_5})N}$ (29)^a



^{*a*}[Ti] = CpTi{PhC(NⁱPr)₂}; Ar^{F₅} = C₆F₅.

difference in Ti– $N_{metallacycle}$ distances (1.868(4) and 2.147(3) Å) was comparable with that for **29**.

Scheme 6 illustrates two alternative routes for the formation of **29** from **26**. Both begin by the [2 + 2] cycloaddition of $Ar^{F_5}CN$ to $Ti=N_{\alpha}$ of **26** to form the azametallacyclobutene intermediate **29_int1**, as found in both titanium imido and hydrazido chemistry.^{8r,42} Insertion of another 1 equiv of $Ar^{F_5}CN$ into the new $Ti-N(CAr^{F_5})$ bond would lead directly to **29**. On the other hand, ring opening via **29_int2** and [2 + 2]cycloaddition (to form **29_int3**), followed by isomerization, would also afford **29**. An analogous mechanism was proposed for the formation of $Cp^*Ti\{MeC(N^iPr)_2\}\{N(NCPh_2)C(Ar^{F_5})-NC(Ar^{F_5})N\}$ from **14**. However, when the reaction was followed by ¹H NMR spectroscopy, no intermediates were seen prior to **29** and therefore which of the two pathways is operative cannot be identified.

Reactions with Alkynes. As mentioned in the Introduction, reactions of group 4 imides and hydrazides with alkynes has been a topic of continuing interest for over 20 years, producing a range of new C–N bond forming reactions, some of which are catalytic.^{1a-f,4,7,8c,d,f,h,i,l,n,p,v,9i,m,o,34k,40e,47} In the case of terminal alkynes, there is also the possibility of competitive 1,2-C–H bond activation across the M=NR bond.^{10d,21,47d,48} Of particular relevance are the N_{α}–N_{β} bond reductive cleavage reactions^{8h,p,9m,12} available for hydrazides. As mentioned above, the only previously reported reaction of a group 4 alkoxyimido complex with alkynes is that of Ti(N₂N^{Me})(NO^tBu)(py) (6) with PhCCMe, forming 7 (Figure 2) via N–O bond cleavage.^{14a}

Disappointingly, no reactions were observed between $Cp*Ti\{MeC(N^iPr)_2\}(NO^iBu)$ (15) and alkynes such as PhCCMe and $Ar^{CF_3}CCMe$ ($Ar^{CF_3} = 4 \cdot C_6H_4CF_3$). NMR tube scale reactions of $Ar^{CF_3}CCH$ and 19 gave complicated mixtures. In contrast, the reaction of $Ar^{F_3}CCH$ with 19 in C_6D_6 resulted in a purple solution and a single product, $Cp*Ti(O^iBu)\{NC-(Ar^{F_3})C(H)N(^iPr)C(Ph)N(^iPr)\}$ (30), after 16 h at room temperature (Scheme 7). Compound 30 was isolated in 80% yield upon scale-up.

The ¹H, ¹³C, and ¹⁹F NMR spectra for **30** revealed a C_1 -symmetric species with two inequivalent ⁱPr groups, resonances attributable to Ph, Cp*, and C₆F₅ groups (with five inequivalent F environments at 223 K due to restricted rotation), and a

 $\begin{array}{l} \label{eq:scheme 7. Reaction of Cp*Ti{PhC(N^iPr)_2}(NO^tBu) \ (19) \\ \mbox{with } Ar^{F_s}CCH \ \mbox{and Proposed Mechanism of Formation for} \\ Cp*Ti(O^tBu)\{NC(Ar^{F_s})C(H)N(^iPr)C(Ph)N(^iPr)\} \ (30) \\ \end{array}$



singlet at δ 6.86 ppm of relative intensity 1 H in the ¹H NMR spectrum assigned to the incorporated alkyne moiety. At first sight the NMR data appear to indicate formation of the [2 + 2]cycloaddition product 30 int1 (or its isomer with CAr^{F5} bound to Ti) depicted in Scheme 7, analogous to the case for $Cp*Ti{PhC(N^{i}Pr)_{2}}{SC(S)N(O^{t}Bu)}$ (20) and $Cp*Ti{PhC (N^{i}Pr)_{2}$ {OC(NAr')N(O^tBu)} (21) and the metallacyclobutene species formed between Ar^{Fs}CCH and 14, Cp*Ti{MeC- $(N^{i}Pr)_{2}$ {N(NCPh₂)C(Ar^{F₅})C(H)} (31).^{10f} However, the shift of δ 6.86 ppm for the alkyne-derived CCH is at much higher field than is usually found for such [2 + 2] cycloaddition products (for example δ 9.19 ppm in the case of **31**).^{8p,r,21,44a,47e,49} In addition, the ¹³C resonances for the HCCAr^{F₅} residue (δ 138.9 and 108.8 ppm, respectively) are also inconsistent with the formation of a cycloaddition product (δ 167.8 and 140.3 ppm for 31 by way of example). Most importantly, a ¹H-¹³C HMBC experiment (Figure S5 in the Supporting Information) revealed coupling of the HCCAr^{F5-}

derived hydrogen with one of the isopropyl group NC(H)-MeMe carbons and also between NC(H)MeMe and HCCAr^{F₅}. A ¹H ROESY NMR experiment also showed through-space interactions between one NC(H)MeMe and HCCAr^{F₅}. Considering these NMR data, the product is assigned as Cp*Ti(O^tBu){NC(Ar^{F₅})C(H)N(ⁱPr)C(Ph)N(ⁱPr)} (**30**; Scheme 7).

The mechanism of formation of **30** is probably similar to that previously described for the formation of 7 and 9 (Figure 2) and recent hydrazide reactions involving azirinyl intermediates.^{8p,9i,m,12,14a} Thus, initial cycloaddition (**30_int1**) precedes $N_{\alpha}-O_{\beta}$ bond cleavage and formation of an azirinyl intermediate (**30_int2**). This in turn undergoes nucleophilic attack by one of the amidinate nitrogens. Noninnocent behavior of an amidinate ligand in these types of complexes is not unprecedented, having previously been observed in the reaction of Cp*Ti{MeC(NⁱPr)₂}(N^tBu) (**10**) with CS₂, which involves insertion of CS₂ into a Ti–N_{amidinate} bond to generate the crystallographically authenticated [Cp*Ti{N(ⁱPr)C(Me)N-(ⁱPr)C(S)S}(μ -S)]₂ (**32**).^{22d}



Unfortunately, while the reaction of **19** shows that reductive cleavage of the alkoxyimido $N_{\alpha}-O_{\beta}$ bond is possible with the appropriate alkyne, treatment with CO or the isonitriles XylNC or 'BuNC (reagents that are known to induce $N_{\alpha}-N_{\beta}$ bond cleavage in a number of hydrazido compounds^{7,8r,9a}) led to the formation of complex and unknown mixtures and these reactions were not investigated further.

Alkylation, Protonation, and Related Reactions. Since the discovery that group 6 hydrazide compounds were found to be possible intermediates in the reduction of dinitrogen to ammonia,⁵⁰ reactions of these complexes with proton sources and alkylating agents have been intensely explored.13c,d,51 Reactions with alkyl halides resulted in alkylation at N_{β} , whereas protonation reactions resulted in reaction at either \dot{N}_{α} or N_b. Although analogous reactions with group 4 hydrazides are much more limited,^{8c,j} a recent detailed study from our group showed that reaction of $Cp*Ti\{MeC(N^{i}Pr)_{2}\}(NNMe_{2})$ (13) with alkyl halides (MeI, EtI, and PhCH₂Br) resulted exclusively in alkylation at N_{β} , whereas protonation with $[Et_3NH][BPh_4]$ gave exclusively protonation of N_{α} .^{8t,w} So as to understand better the nature of the group 4 M=NO^tBu group, reactions of 19 with a number of potential Brønsted and Lewis acids were carried out.

Reactions of **19** with the alkylating agents MeI, $[Me_3O]$ - $[BF_4]$, and Me_2SO_4 were disappointing, ultimately resulting in unknown mixtures. Reaction with $[HNEt_3][BPh_4]$ in THF- d_8 required 2 equiv to reach completion, yielding a new set of resonances in the ¹H NMR spectrum consistent with NEt₃ and apparently a new titanium complex. Removal of the THF- d_8 and NEt₃ byproducts and redissolving the remaining solid in C_6D_5Br resulted in diffraction-quality colorless crystals. Single-

crystal X-ray diffraction showed these to be $[PhC(N^{i}PrH)_{2}]$ -[BPh₄] (**33-BPh**₄; eq 3).



The molecular structure and selected bond lengths and angles are given in Figure S6 and Table S3 of the Supporting Information, and the metric data are within the expected ranges. Compound **33-BPh**₄ was independently synthesized via anion exchange between [PhC(NⁱPrH)₂]Cl and Na[BPh₄] and isolated in 63% yield. [Cp*Ti(NO^tBu)(THF)₂][BPh₄] (**34-BPh**₄; eq 3) is formed alongside **33-BPh**₄. Attempts to isolate **34-BPh**₄ on scale-up as either the THF or bipy adduct (to form a less labile species) were unsuccessful. However, direct evidence for **34**⁺ was found using positive ion electrospray mass spectrometry for a solution of **33** and **34** generated in situ in THF-*d*₈. Complexes with both one and two coordinated THF molecules were identified in the mass spectrum with the correct isotope distribution (*m*/*z* 343 and 415, respectively).

Group 4 hydrazides $M(N_2^{R}N^{py})(NNPh_2)(py)$ are known to readily form zwitterionic N_{α} adducts of the type $M(N_2^{R}N^{py})$ - $\{\eta^2 \cdot N(NPh_2)B(Ar^{F_5})_3\}$ (35; $N_2^{R}N^{py} = (2 \cdot NC_5H_4)CMe-(CH_2NR)_2$; M = Ti, $R = SiMe_3$ (a); M = Zr (b), Hf (c), $R = SiMe_2^{TB}U$) with $B(Ar^{F_5})_3$.^{8r,9b} On the other hand, although 13 showed no apparent reactivity toward $B(Ar^{F_5})_3$,^{8w} it was hoped that the corresponding reaction of 19 with $B(Ar^{F_5})_3$ might nevertheless provide additional insight into the chemistry of the alkoxyimido functional group.



Compound **19** reacted very slowly with 1 equiv of $B(Ar^{F_5})_3$ in C_6D_6 at room temperature, giving less than 10% conversion to a new compound, $Cp^*Ti\{PhC(N^iPr)_2\}\{\eta^2-ON(H)B(Ar^{F_5})_3\}$ (**36**), after 24 h. Heating for 5 days at 70 °C drove the reaction to ca. 70% completion, and use of an excess of borane also effected complete conversion at room temperature after 2 days (after which time the excess borane remained unreacted). When the reaction was monitored by ¹H NMR, isobutene was also formed (either at room temperature or at 70 °C) alongside **36**, as judged by multiplet and triplet (⁴J = 1.2 Hz) resonances at δ 4.74 (2 H) and 1.58 (6 H) ppm.⁵² The reaction was scaled up in benzene at 70 °C for 16 h to give **36** as an orange crystalline solid whose identity was confirmed by single-crystal X-ray diffraction. The molecular structure is shown in Figure 10, and selected bond lengths and angles are given in Table 5.



Figure 10. Displacement ellipsoid plot (20% probability) of Cp*Ti{PhC(NⁱPr)₂}{ η^2 -ON(H)B(Ar^{F₅})₃} (36). C-bound H atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{*}Ti\{PhC(N^{i}Pr)_{2}\}\{\eta^{2}-ON(H)B(Ar^{F_{5}})_{3}\}$ (36)^{*a*}

Ti(1)-Cp _{cent}	2.063	Ti(1) - F(1)	2.2903(8)	
Ti(1) - N(1)	2.1242(12)	N(1)-B(1)	1.5850(18)	
Ti(1) - N(2)	2.1620(11	N(1) - O(1)	1.4392(14)	
Ti(1) - N(3)	2.0576(11)	C(25)-F(1)	1.3814(16)	
T(1)-O(1)	1.8549(10)			
Cp_{cent} -Ti(1)-N(1)	147.04	N(2)-Ti(1)-N(3)	63.23(4)	
Cp_{cent} -Ti(1)-N(2)	116.16	N(1)-Ti(1)-O(1)	41.72(4)	
Cp_{cent} - $Ti(1)$ - $N(3)$	110.77	Ti(1)-N(1)-O(1)	59.07(6)	
Cp_{cent} - $Ti(1)$ - $O(1)$	106.97	Ti(1) - O(1) - N(1)	79.21(6)	
Cp_{cent} - $Ti(1)$ - $F(1)$	101.30	Ti(1)-N(1)-B(1)	139.51(9)	
Cp _{cent} is the computed centroid for the Cp* ring carbons.				

Compound **36** is a half-sandwich titanium complex with η^{5} - $C_{5}Me_{5}$, $\kappa^{2}N,N'$ amidinate, and η^{2} -ON(H)B(Ar^{F₅})₃ ligands as well as a Ti…F interaction between the metal and an o- $C_{6}F_{5}$ fluorine atom. The distances and angles associated with the Cp*Ti{PhC(NⁱPr)₂} fragment are unexceptional, and so we focus on the ON(H)B(Ar^{F₅})₃ moiety, which formally comprises a HNO (nitroxyl) ligand⁵³ additionally N-bound to B(Ar^{F₅})₃. Four structurally characterized complexes containing HNO as a ligand, with either η^{2} (one example) or η^{1} (three examples, all

N-bound) coordination, and over 20 with N-substituted η^2 -ON(H)R ligands (average N-O distance 1.396 Å, range 1.371–1.498 Å) have been reported, all for transition metals in groups $5-9.^{27}$ With respect to titanium, seven Ti(+4) complexes with η^2 -ON(R)R' ligands (R, R' = alkyl) have been structurally authenticated (average distances (range): N-O = 1.429 (1.402–1.446), Ti–O = 1.912 (1.872–1.980), Ti– N = 2.128 (2.095–2.230) Å):²⁷ for example, Ti(η^2 -ONMe₂)₄ and Cp*TiMe₂{ η^2 -ON(^tBu)Me}.⁵⁴ The Ti(1)–O(1), Ti(1)– N(1), and N(1)-O(1) distances for 36 lie near to or within these ranges. The N(1)-B(1) bond length of 1.5850(18) Å in **36** is comparable to those in $M(N_2^R N^{py}) \{\eta^2 - N(NPh_2)B(Ar^{F_3})\}$ $(35; 1.562(3)-1.598(3) \text{ Å})^{8r,9b}$ and also, for example, [B- $(Ar^{F_5})_3(N_3)$]⁻ (1.583(2) Å),⁵⁵ Ti(NEt₂)₃{NH₂B(Ar^{F₅})₃} (1.595(3) Å), and CpTi(NMe₂)₂{NH₂B(Ar^{F₅})₃} (1.598(2) Å).⁵⁶ The Ti(1)…F(1) interaction in 36 (2.2903(8) Å, which is less than the sum of the van der Waals radii of 3.92 Å⁵⁷) is electrostatic in nature and presumably augmented by the formal positive charge on titanium. A similar Ti-F interaction was found in $Ti(N_2^{SiMe3}N^{py}){\eta^2-N(NPh_2)B(Ar^{F_5})_3}$ (35a),^{8r} albeit with a slightly longer distance of 2.4840(15) Å. Also, as found in 35a, there is a small but significant lengthening of the C(25)-F(1) bond (1.3814(16) Å) in comparison to the other aryl C-F bond lengths (range 1.3361(17)-1.3565(16) Å). Taken together, these structural parameters are consistent with the zwitterionic representation of 36 shown in Scheme 8. Furthermore, 36 is therefore the first fully authenticated nitroxyl complex of a group 4 metal, stabilized by borane coordination.

The spectroscopic data for 36 are consistent with the solidstate structure. The ¹H and ¹³C data are indicative of a C_1 symmetric complex containing Cp* and PhC(NⁱPr)₂ ligands, but no tert-butyl group, this being the source of the eliminated isobutene. A signal at δ 6.05 ppm is assigned to the N-bound hydrogen, and the IR spectrum shows a ν (N–H) band at 3296 cm⁻¹. The ¹¹B NMR spectrum shows as resonance at δ –8 ppm, consistent with a tetracoordinate boron.⁵⁸ Note that at room temperature no exchange between free and coordinated $B(Ar^{F_5})_3$ is observed on the NMR time scale. The ¹⁹F NMR spectrum of pure 36 is broad at room temperature, but cooling to -20 °C shows 13 separate fluorine environments. Examination of the relative intensities and changes in appearance on warming to room temperature establishes that, at -20 °C, two of the C₆F₅ rings display restricted rotation on the NMR time scale whereas one is able to rotate relatively freely. From the appropriate coalescence points the activation free energies for exchange within and between the rings were found to be comparable within error ($\Delta G^{\ddagger} = 13.1(1)$ and 12.7(1) kcal mol⁻¹ at 291 and 268 K, respectively), indicating a geared process as illustrated in Scheme 8.59

Scheme 8. Mechanism for Ar^{F_5} Ring Exchange in $Cp^*Ti\{PhC(N^iPr)_2\}\{\eta^2-ON(H)B(Ar^{F_5})_3\}$ (36)



Scheme 9. Reaction of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19) with B(Ar^{F₅})₃ and Proposed Mechanism for formation of Cp*Ti{PhC(NⁱPr)₂}{ η^2 -ON(H)B(Ar^{F₅})₃} (36)



A proposed mechanism for the formation of 36 is given in Scheme 9. Since 19 itself is thermally stable at 70 °C for several days in solution, we propose that isobutene elimination is preceded by borane coordination to the alkoxyimido nitrogen in a manner analogous to that in $M(N_2^R N^{py}) \{\eta^2 - N(NPh_2)B$ - $(Ar^{F_5})_3$ (35). This generates a formally zwitterionic species, potentially with coordination of the O-tert-butyl group to the formally cationic metal center, depicted as 36 int. Indeed, isobutene elimination is not uncommon from cationic group 4 complexes containing either tert-butoxy ligands⁶⁰ or ligands with -O^tBu substituents such as Carpentier's cationic *tert*-butyl enolate systems.^{52a,61} Subsequent intramolecular hydrogen transfer to nitrogen leads to alkene elimination and formation of the new borane-stabilized nitroxyl ligand. Finally we note that, whereas AlMe₃ readily coordinates to the oxygen atom of $Cp*TiMe_2(\eta^2-ONEt_2)$ to form $Cp*TiMe_2\{\eta^2-O(AlMe_3) NEt_2$,⁶² excess $B(Ar^{F_5})_3$ does not coordinate to the nitroxyl oxygen of 36.

CONCLUSIONS

We have reported the first use of imide/alkoxyamine exchange to synthesize new alkoxyimido complexes, namely Cp*Ti- ${MeC(N^{i}Pr)_{2}}(NO^{t}Bu)$ (15) and $Cp*Ti{PhC(N^{i}Pr)_{2}}$ -(NO^tBu) (19). Following this, the first thorough investigation into the reactions of alkoxyimido complexes with small unsaturated molecules was undertaken. The reaction outcomes are reminiscent of those seen with imido and diphenyl-, dimethyl-, and alkylidenehydrazido compounds. Although reaction with CO2 produced complicated mixtures, addition of CS₂ gave the stable cycloaddition product Cp*Ti{PhC- $(N^{i}Pr)_{2}$ {SC(S)N(O^tBu)} (20). The reactions of 19 with isocyanates were dependent on the steric bulk of the isocyanate substituent. Thus, with Ar'NCO the cycloaddition product $Cp*Ti{PhC(N^{i}Pr)_{2}}{N(O^{t}Bu)C(NAr')O}$ (21) was isolated, with TolNCO 2 equiv was needed to synthesis the "rearrangeddouble insertion" product $Cp*Ti{PhC(N^iPr)_2}{OC(NTol)N-}$ $(Tol)C(NO^{t}Bu)O$ (22), and finally with ^tBuNCO the carbodiimide derivative ^tBuONCN^tBu (24) was formed following extrusion from the unstable cycloaddition intermediate. Cycloaddition-extrusion reaction pathways were also seen with aldehydes and ketones, generating the oxo dimer 23 and corresponding oxime ethers PhC(NO^tBu)H (25a) and PhC(NO^tBu)Me (25b) as a mixture of geometric isomers. DFT calculations showed that the product distribution was attributed to the energy barrier to cycloaddition formation. The reaction also yielded the new oxime ether PhC(NO^tBu)Ph (25c) in high yield, which was inaccessible following alternative routes. Reactions of 19 with Ar^{F5}CN and Ar^{F2}CN led to the net Ar^{F₅}CN, the unusual insertion compound $Cp^{*}Ti{PhC(N^{i}Pr)_{2}}$ -

{NC(Ar^{F₅})NC(Ar^{F₅})N(C{Ar^{F₅}}NO^tBu)} (29) was formed. Reactions with both Ar^{F₅}CCH and [HNEt₃][BPh₄] led to reactions involving the amidinate supporting ligand, with the reaction using Ar^{F₅}CCH inducing N_{α}-O_{β} bond cleavage and that with [HNEt₃][BPh₄] giving protonation of the amidinate ligand. Finally reaction with B(Ar^{F₅})₃ resulted in loss of isobutene to give Cp*Ti{PhC(NⁱPr)₂}{ η^2 -ON(H)B(Ar^{F₅})₃} (36), the first example of a HNO (nitroxyl) adduct for a group 4 metal (with B(Ar^{F₅})₃ stabilization).

EXPERIMENTAL SECTION

Representative syntheses are given below. Further information is given in the Supporting Information.

Cp*Ti{PhC(N'Pr)₂}(NO^tBu) (19). To a solution of Cp*Ti{PhC- $(N^{i}Pr)_{2}$ (N^tBu) (18; 7.67 g, 16.8 mmol) in Et₂O (15 mL), cooled to -78 °C, was added ^tBuONH₂ in toluene (1.8 M, 13.0 mL, 23.5 mmol) and the solution was slowly warmed to room temperature. A color change from red to dark green-black was observed. After 3.5 h the volatiles were removed under reduced pressure to afford 19 as a dark green oil, which was triturated in hexane (25 mL) and filtered. The resultant green solid was then washed with cold hexane $(3 \times 15 \text{ mL})$, cooled to -78 °C, filtered, and dried in vacuo. Yield: 5.56 g (70%). Diffraction-quality crystals were grown from a saturated hexane solution slowly cooled to -80 °C. ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.51 (1 H, d, ³J = 8.1 Hz, o_a -C₆H₅), 7.23-7.07 (4 H, m, overlapping o_b -C₆H₅, m-C₆H₅ and p-C₆H₅), 3.66 (2 H, sept, ${}^{3}J = 6.3$ Hz, NCHMeMe), 2.21 (15 H, s, C_5Me_5), 1.15 (9 H, s, NOCMe₃), 1.02 (6 H, d, ${}^{3}J$ = 6.3 Hz, NCHMeMe), 0.91 (6 H, d, ${}^{3}J$ = 6.3 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 164.8 (PhCN₂), 135.1 (*i*-C₆H₅), 128.9, 128.6, 128.3 (*p*-C₆H₅, *m*-C₆H₅, *o*_b- C_6H_5), 127.7 (o_a - C_6H_5), 119.5 (C_5Me_5), 80.4 (NOCMe₃), 49.9 (NCHMeMe), 27.0 (NOCMe₃), 26.8 (NCHMeMe), 25.6 (NCHMeMe), 12.1 (C5Me5) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1642 (w), 1357 (s), 1336 (s), 1260 (m), 1222 (m), 1168 (m), 1142 (s), 1076 (w), 1017 (m), 845 (m), 783 (w), 750 (m), 737 (m), 707 (s). EI-MS: m/z 473 $[M]^+$ (2%). Anal. Found (calcd for C₂₇H₄₃N₃OTi): C, 68.61 (68.49); H, 9.17 (9.15); N, 8.58 (8.87).

Cp*Ti{PhC(NⁱPr)₂}(SC(S)N(O^tBu)) (20). To a solution of Cp*Ti- ${PhC(N^{i}Pr)_{2}}(NO^{t}Bu)$ (19; 0.250 g, 0.528 mmol) in benzene (5 mL) was added CS₂ (38.1 μ L, 0.634 mmol), all at room temperature. A color change from green to dark brown was observed. After 6 h the volatiles were removed under reduced pressure to afford 20 as a dark brown oily solid, which was then triturated with pentane (5 mL) and filtered; the resultant brown powder was dried in vacuo. Yield: 0.190 g (65%). ¹H NMR (toluene- d_{87} 499.9 MHz, 223 K): δ 6.97 (2 H, m, o-C₆H₅), 6.91 (1 H, m, p-C₆H₅), 6.72 (2 H, m, m-C₆H₅), 3.36 (2 H, m, overlapping NCH_aMeMe and NCH_bMeMe), 2.02 (15 H, s, C₅Me₅), 1.54 (9 H, s, NOCMe₃), 0.98 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_aMeMe), 0.95 $(3 \text{ H}, \text{ d}, {}^{3}J = 6.5 \text{ Hz}, \text{ NCH}_{a}\text{MeMe}), 0.89 (3 \text{ H}, \text{ d}, {}^{3}J = 6.5 \text{ Hz},$ NCH_bMeMe), 0.85 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe) ppm. ${}^{13}C{}^{1}H{}$ NMR (toluene-d₈, 125.7 MHz, 223 K): δ 167.3 (PhCN₂), 148.1 (SC(S)N), 132.6 (i-C₆H₅), 131.2 (C₅Me₅), 129.6 (o_a-C₆H₅), 129.0 (p- C_6H_5), 128.7 ($o_b-C_6H_5$), 128.5 ($m_a-C_6H_5$), 128.1 ($m_b-C_6H_5$), 78.6 (NOCMe₃), 51.7 (NCH_bMeMe), 51.6 (NCH_aMeMe), 28.7 (NOCMe₃), 25.7 (NCH_bMeMe), 25.6 (NCH_bMeMe), 25.16, 25.17

(overlapping NCH_aMeMe and NCH_aMeMe), 14.5 (C_5Me_5) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1639 (w), 1359 (s), 1330 (s), 1217 (m), 1197 (s), 1170 (m), 1142 (m), 1120 (m), 1103 (m), 1075 (w), 1040 (w), 1019 (m), 987 (w), 928 (s), 910 (s), 860 (w), 781 (s), 711 (m). Anal. Found (calcd for $C_{28}H_{43}N_3OS_2Ti$): C, 61.37 (61.18); H, 7.74 (7.89); N, 7.82 (7.64).

Cp*Ti{PhC(NⁱPr)₂}{OC(NAr')N(O^tBu)} (21). To a solution of $Cp*Ti{PhC(N^{i}Pr)_{2}}(NO^{t}Bu)$ (19; 0.320 g, 0.676 mmol) in $Et_{2}O$ (5 mL) was added Ar'NCO (144 µL, 0.676 mmol), all at room temperature. An immediate color change from green to red-brown was observed. After 3.5 h, the volatiles were removed under reduced pressure to afford 21 as a dark brown solid, which was then triturated with hexane (5 mL) at -30 °C and filtered; the resultant brown powder was dried in vacuo. Yield: 0.184 g (40%). ¹H NMR (toluene d_{8} , 499.9 MHz, 243 K): δ 7.59 (1 H, d, ${}^{3}J = 7.5$ Hz, o_{a} -C₆H₅), 7.31 (1 H, d, ${}^{3}J = 7.5$ Hz, o_{b} -C₆H₅), 7.22-7.00 (5 H, m, m-C₆H₅, m-2,6- $C_6H_3^{i}Pr_{2}$, p-2,6- $C_6H_3^{i}Pr_2$), 6.88 (1 H, m, p- C_6H_5), 3.73 (1 H, sept, ³J = 6.5 Hz, NCH_aMeMe), 3.64 (1 H, br sept, 2,6-C₆H₃(CH_aMeMe)₂), 3.18 (1 H, br sept, 2,6-C₆H₃(CH_bMeMe)₂), 3.06 (1 H, sept, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 2.08 (15 H, s, C₅Me₅), 1.75 (3 H, br d, 2,6-C₆H₃(CH_aMeMe)₂), 1.64 (3 H, br d, 2,6-C₆H₃(CH_bMeMe)₂), 1.50 (9 H, s, NOCMe₃), 1.42 (3 H, br d, $2,6-C_6H_3(CH_aMeMe)_2$), 1.27 (3 H, d, ${}^{3}J = 6.5 \text{ Hz}$, NCH_aMeMe), 1.21 (3 H, br d, 2,6-C₆H₃(CH_bMeMe)₂), 0.93 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_aMeMe), 0.63 (6 H, d, ${}^{3}J$ = 6.5 Hz, NCH_bMeMe) ppm. ¹³C{¹H} NMR (toluene- d_{8} , 125.7 MHz, 243 K): δ 170.7 (PhCN₂), 154.4 (OCN), 145.7 (*i*-2,6-C₆H₃ⁱPr₂), 140.0 (*o*_a-2,6- $C_6H_3^{i}Pr_2$), 139.5 (o_b -2,6- $C_6H_3^{i}Pr_2$), 132.9 (*i*- C_6H_5), 129.1, 128.2, 128.5, $(p-2,6-C_6H_3^{i}Pr_2, m_a-C_6H_5 \text{ and } m_b-C_6H_5)$, 128.8 $(o_a-C_6H_5)$ overlapping with solvent), 128.6 (C5Me5 overlapping with solvent), 127.5 $(p-C_6H_5)$, 122.6 $(o_b-C_6H_5)$, 121.6 $(m_b-2,6-C_6H_3^{-1}Pr_2)$, 121.3 $(m_a-2,6-C_6H_3^{-1}Pr_2)$ 2,6-C₆H₃ⁱPr₂), 80.8 (NOCMe₃), 50.5 (NCH_aMeMe), 50.3 (NCH_bMeMe), 29.5 (2,6-C₆H₃(CH_aMeMe)₂), 28.5 (overlapping NOCMe₃ and 2,6-C₆H₃(CH_bMeMe)₂), 27.5 (NCH_bMeMe), 26.5 $(NCH_{a}MeMe)$, 26.2 $(NCH_{a}MeMe)$, 25.1 $(2,6-C_{6}H_{3}(CH_{a}MeMe)_{2})$, 23.8 $(2,6-C_6H_3(CH_aMeMe)_2)$, 23.6 $(2,6-C_6H_3(CH_bMeMe)_2)$, 23.2 (NCH_bMeMe), 21.5 (2,6-C₆H₃(CH_bMeMe)₂), 12.9 (C₅Me₅) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1631 (s), 1583 (s), 1510 (m), 1394 (s), 1359 (s), 1335 (s), 1220 (m), 1188 (m), 1148 (m), 1119 (m), 1102 (w), 1066 (m), 1045 (m), 1022 (m), 973 (m), 936 (w), 858 (w), 832 (w), 790 (m), 782 (m), 753 (w), 730 (s), 705 (m), 681 (w), 555 (w). Anal. Found (calcd for C₄₀H₆₀N₄O₂Ti): C, 71.04 (70.99); H, 8.73 (8.94); N, 8.06 (8.28)

Cp*Ti{PhC(NⁱPr)₂}{OC(NTol)N(Tol)C(NO^tBu)O} (22). To a solution of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19; 0.250 g, 0.528 mmol) in benzene (10 mL) was added TolNCO (140 μ L, 1.11 mmol), all at room temperature. An immediate color change from green to brownred was observed. After 2.5 h, the volatiles were removed under reduced pressure to afford 22 as a light brown crystalline solid. Pentane (10 mL) was added and the solution concentrated by half before cooling to -80 °C. The resulting solid was then isolated by filtration and the red-brown powder dried in vacuo. Yield: 0.235 g (60%). Diffraction-quality crystals were grown from a saturated Et₂O solution at 4 °C. ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.72 (2 H, d, ${}^{3}J$ = 8.1 Hz, o_{a} -C₆H₄Me), 7.39 (2 H, d, ${}^{3}J$ = 7.5 Hz, o-C₆H₅), 7.16 (2 H, m, ob-C6H4Me), 7.06-7.00 (7 H, m, overlapping m-C6H5, p- C_6H_5 , $m_a-C_6H_4Me$, $m_b-C_6H_4Me$), 3.67 (2 H, overlapping sept, NCH_aMeMe and NCH_bMeMe), 2.20 (3 H, s, p_b-C₆H₄Me), 2.12 (3 H, s, p_a - C_6H_4Me), 1.99 (15 H, s, C_5Me_5), 1.49 (3 H, d, ${}^{3}J$ = 6.6 Hz, NCH_aMeMe), 1.10 (9 H, s, NOCMe₃), 1.05 (3 H, d, ${}^{3}J$ = 6.9 Hz, NCH_bMeMe), 0.96 (3 H, d, ${}^{3}J$ = 6.6 Hz, NCH_aMeMe), 0.91 (3 H, d, ${}^{3}J$ = 6.9 Hz, NCH_bMeMe) ppm. ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 75.4 MHz, 293 K): δ 170.4 (PhCN₂), 156.4 (OC_aN), 153.9 (OC_bN), 148.5 (*i*_b-C₆H₄Me), 141.3 (*i*_a-C₆H₄Me), 134.4 (*m*_a-C₆H₄Me), 133.8 (*i*-C₆H₅), 130.3 (C_5Me_5), 129.6, 129.0, 128.3 ($p-C_6H_5$, $m_b-C_5H_4Me$, $m-C_6H_5$), 129.2 $(p_b-C_6H_4Me)$, 129.2 $(o-C_6H_5)$, 128.6 $(p_a-C_6H_4Me)$, 128.5 $(o_a-C_6H_4Me)$, 128.5 (oC₆H₄Me), 124.5 (*o*_b-C₆H₄Me),76.7 (NOCMe₃), 51.2 (NCH_bMeMe), 50.9 (NCH_aMeMe), 27.6 (NOCMe₃), 26.6 (NCH_aMeMe) 25.4 (NCH_bMeMe), 24.8 (NCH_bMeMe), 24.0 (NCH_aMeMe), 21.1 (p_a- C_6H_4Me), 21.1 ($p_b-C_6H_4Me$), 12.8 (C_5Me_5) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1623 (s), 1587 (s), 1575 (s), 1512 (m), 1506 (m),

1422 (m), 1356 (s) 1337 (s), 1279 (w), 1250 (m), 1217 (m), 1195 (m), 1142 (m), 1112 (m), 1103 (w), 1088 (m), 1043 (w), 1021 (m), 1001 (m), 955 (m), 932 (w), 916 (w), 869 (w), 826 (w), 814 (m), 807 (m), 788 (w), 780 (m), 734 (m), 726 (m), 713 (w), 707 (m), 678 (w), 646 (w), 619 (m). EI-MS: m/z 353 [OC(NO'Bu)N(Tol)C-(NTol)O]⁺ (60%). Anal. Found (calcd for C₄₃H₅₇N₅O₃Ti): C, 70.09 (69.81); H, 7.59 (7.77); N, 9.42 (9.47).

Reaction of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) with 'BuNCO: Synthesis of [Cp*Ti{PhC(NⁱPr)₂}(\mu-O)]₂ (23) and 'BuNCNO^tBu (24). To a solution of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19; 0.500 g, 1.06 mmol) in Et₂O (5 mL) was added 'BuNCO (121 \muL, 1.06 mmol), all at room temperature. A color change from green to yellow was observed. After 16 h the solution was filtered, giving 23 as a yellow solid which was dried in vacuo. Yield: 0.289 g (68%). Removal of the volatiles from the filtrate gave 24 as a colorless liquid. Yield: ca. 10%, due to the volatility of 24 itself. Diffraction-quality crystals of 23 were grown from a saturated hexane solution at 4 °C.

Data for [*Cp***Ti*{*PhC*(*NⁱPr*)₂}(*μ*-*O*)]₂ (**23**). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.35 (2 H, m, o-C₆H₅), 7.15 (3 H, m, overlapping *m*-C₆H₅ and *p*-C₆H₅), 3.69 (2 H, sept, ³J = 6.3 Hz, NCHMeMe), 2.28 (15 H, s, C₅Me₅), 1.28 (6 H, d, ³J = 6.6 Hz, NCHMeMe), 1.09 (6 H, d, ³J = 6.3 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 172.0 (PhCN₂), 137.0 (*i*-C₆H₅), 128.3, 128.2, 127.9 (overlapping with solvent *p*-C₆H₅, *m*-C₆H₅), *n*-C₆H₅), 122.7 (C₅Me₅), 48.4 (NCHMeMe), 26.2 (NCHMeMe), 25.6 (NCHMeMe), 13.7 (C₅Me₅) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1419 (m), 1359 (m), 1323 (s), 1261 (w), 1210 (m), 1165 (m), 1141 (m), 1108 (w), 1014 (m), 938 (w), 799 (w), 780 (m), 738 (w), 707 (m), 637 (s), 597 (m). EI-MS: *m*/z 669 [*M* − Cp^{*}]⁺ (2%), 402 [Cp*Ti{PhC(NⁱPr)₂}-(O)]⁺ (90%). Anal. Found (calcd for C₄₆H₆₈N₄O₂Ti₂): C, 68.78 (68.65); H, 8.87 (8.52); N, 6.81 (6.96).

Data for ¹BuNCNO^tBu (**24**). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 1.25 (9 H, s, NOCMe₃), 1.05 (9 H, s, NCMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 154.7 (NCN), 79.2 (NOCMe₃), 57.8 (NCMe₃), 30.4 (NCMe₃), 27.1 (NOCMe₃) ppm. Solution IR (NaCl plates, Et₂O, cm⁻¹): 2257 (m), 2065 (s). FI-HRMS found (calcd for C₉H₁₈N₂O): *m/z* 170.1421 (170.1419).

PhC(NO^tBu)H (25a). To a solution of Cp*Ti{PhC(NⁱPr)₂}-(NO^tBu) (19; 0.250 g, 0.528 mmol) in C₆H₆ (5 mL) was added PhC(O)H (53.7 μ L, 0.528 mmol), all at room temperature. An immediate color change to yellow was observed. After 30 min the volatiles were removed under reduced pressure and the resulting solid sublimed (80–110 °C, 8 × 10⁻² mbar, 2 h) onto a dry ice/acetone cold finger, yielding 25a as a colorless oil at room temperature. Yield: 0.066 g (70%). The ¹H NMR spectrum indicated an approximately 20:80 mixture of the *syn* and *anti* isomers.

Major lsomer (anti). ¹H NMR (C_6D_6 , 299.9 MHz, 293 K): δ 7.85 (2 H, d, o- C_6H_5), 7.27 (1 H, s, PhC(H)), 7.15–7.00 (3 H, m, overlapping *m*- C_6H_5 and *p*- C_6H_5), 1.39 (9 H, s, CMe₃) ppm. ¹³C{¹H} NMR (C_6D_6 , 75.4 MHz, 293 K): δ 144.7 (PhC(H)), 132.0 (*i*- C_6H_5), 131.2 (*o*- C_6H_5), 129.6 (*p*- C_6H_5), 128.5 (*m*- C_6H_5), 79.4 (CMe₃), 27.6 (CMe₃) ppm.

Minor Isomer (syn). The ¹H NMR spectrum was consistent with the literature values.^{36b} ¹H NMR (C_6D_{6i} 299.9 MHz, 293 K): δ 8.03 (1 H, s, PhC(H)), 7.45 (2 H, d, o- C_6H_5), 7.15–7.00 (3 H, m, overlapping m- C_6H_5 and p- C_6H_5), 1.38 (9 H, s, CMe₃) ppm. ¹³C{¹H} NMR (C_6D_{6i} 75.4 MHz, 293 K): δ 147.4 (PhC(H)), 133.8 (*i*- C_6H_5), 129.4 (*p*- C_6H_5), 128.8 (*m*- C_6H_5), 127.1 (*o*- C_6H_5), 79.0 (CMe₃), 27.8 (CMe₃) ppm.

Common Data. IR (thin film, cm⁻¹): 3095 (w), 3058 (w), 3026 (w), 2975 (br, s), 2929 (br, m), 2868 (w), 1636 (m), 1491 (m), 1472 (w), 1448 (m), 1387 (m), 1364 (s), 1318 (w), 1297 (w), 1262 (m), 1190 (m), 1183 (m), 1101 (w), 1078 (w), 1031 (w), 950 (s), 933 (m), 915 (m), 882 (w), 839 (w), 819 (w), 806 (w), 757 (m), 692 (s), 629 (m). FI-HRMS found (calcd for $C_{11}H_{15}NO$): m/z 177.1152 (177.1154).

PhC(NO^tBu)Me (25b). To a solution of Cp*Ti{PhC(NⁱPr)₂}-(NO^tBu) (19; 0.200 g, 0.423 mmol) in C₆H₆ (5 mL) was added PhC(O)Me (49.3 μ L, 0.423 mmol), all at room temperature. A color change from green to yellow was observed. After 30 min the volatiles

were removed under reduced pressure and the resulting solid was sublimed (80–110 °C, 8 × 10⁻² mbar, 2 h) onto a dry ice/acetone cold finger, giving **25b** as a yellow liquid at room temperature. Yield: 0.061 g (75%). The ¹H NMR spectrum indicated an approximately 9:1 mixture of the *syn* and *anti* isomers and was consistent with the literature values.^{36e}

Major Isomer (syn). ¹H NMR (CDCl₃, 499.9 MHz, 293 K): δ 7.69 (2 H, d, ³*J* = 8.0 Hz, *o*-C₆H₅), 7.38–7.33 (3 H, m, overlapping *m*-C₆H₅ and *p*-C₆H₅), 2.22 (Me), 1.37 (9 H, s, CMe₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125.7 MHz, 298 K): δ 152.5 (PhC(Me)), 137.7 (*i*-C₆H₅), 128.7 (*p*-C₆H₅), 128.4 (*m*-C₆H₅), 126.0 (*o*-C₆H₅), 78.8 (CMe₃), 27.9 (CMe₃), 12.4 (Me) ppm.

Minor lsomer (anti). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 7.59 (2 H, m, o-C₆H₅), 7.39–7.31 (3 H, m, overlapping *m*-C₆H₅ and *p*-C₆H₅), 2.21 (Me), 1.30 (9 H, s, CMe₃) ppm. ¹³C{¹H} NMR (CDCl₃, 125.7 MHz, 293 K): δ 151.2 (PhC(Me)), 135.0 (*i*-C₆H₅), 128.6 (*p*-C₆H₅), 128.5 (*o*-C₆H₅), 127.9 (*m*-C₆H₅), 78.2 (CMe₃), 27.6 (CMe₂), 21.9 (Me) ppm.

Cp*Ti{PhC(NⁱPr)₂}{NC(Ar^{F5})NO^tBu} (26). To a solution of Cp*Ti-{PhC(NⁱPr)₂}(NO^tBu) (19; 0.230 g, 0.486 mmol) in benzene (10 mL) was added Ar^{F₅}CN (61.2 μ L, 0.486 mmol), all at room temperature. An immediate color change from green to lime green was observed. After 1 h, the volatiles were removed under reduced pressure to afford 26 as a green oily solid. Et₂O (5 mL) was added and the solution cooled to -80 °C. The resulting green crystalline solid was isolated by filtration and dried in vacuo. Yield: 0.118 g (33%). Diffraction-quality crystals were grown from a saturated hexane solution at -80 °C. ¹H NMR (C₆D₆, 499.9 MHz, 293 K): δ 7.35 (1 H, d, ${}^{3}J = 8.0$ Hz, o_{a} -C₆H₅), 7.12-7.06 (2 H, m, m-C₆H₅), 7.00 (1 H, t, ${}^{3}J$ = 7.5 Hz, p-C₆H₅), 6.93 (1 H, d, ³J = 7.5 Hz, o_b -C₆H₅), 3.40 (2 H, sept, ${}^{3}J = 6.5$ Hz, NCHMeMe), 2.21 (15 H, s, C₅Me₅), 1.40 (9 H, s, NOCMe₃), 0.81 (6 H, d, ${}^{3}J$ = 6.0 Hz, NCHMeMe), 0.77 (6 H, d, ${}^{3}J$ = 6.5 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz, 293 K): δ 166.9 (PhCN₂), 150.1 (NC(C₆F₅)N), 143.2 (2 C, d, ¹J_{C-F} = 244.9 Hz, $o-C_6F_5$), 140.4 (1 C, d, ${}^1J_{C-F}$ = 249.9 Hz, $p-C_6F_5$), 137.8 (2 C, d, ${}^{1}J_{C-F} = 249.1 \text{ Hz}, m-C_{6}F_{5}), 133.1 (i-C_{6}H_{5}), 129.0 (p-C_{6}H_{5}), 128.9 (m-C_{6}H_{5}), 128.9 (m-C_{6}H_{5}$ C_6H_5), 127.4 (o_a - C_6H_5), 127.2 (o_b - C_6H_5), 123.6 (C_5Me_5), 113.2 (1 C, t, ${}^{2}J_{C-F} = 22.4$ Hz, *i*-C₆F₅) 78.0 (NOCMe₃), 50.9 (NCHMeMe), 27.9 (NOCMe₃), 26.4 (NCHMeMe), 24.2 (NCHMeMe), 12.4 (C₅Me₅) ppm. ¹⁹F{¹H} NMR (C₆D₆, 282.1 MHz, 293 K): δ –140.6 (2 F, m, o- C_6F_5), -157.7 (1 F, t, ${}^{3}J$ = 20.6 Hz, p- C_6F_5), -163.9 (2 F, app t, m- C_6F_5) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1651 (w), 1528 (m), 1512 (s), 1492 (s), 1364 (s), 1340 (s), 1294 (m), 1259 (m), 1221 (m), 1194 (m), 1169 (m), 1140 (m), 1108 (m), 1033 (m), 1019 (m), 989 (s), 943 (s), 892 (M), 817 (w), 793 (m), 780 (m), 740 (m), 725 (m), 707 (m), 669 (m), 612 (m), 577 (m). EI-MS: m/z 666 $[M]^+$ (7%). Anal. Found (calcd for C₃₄H₄₃N₄OF₅Ti): C, 61.38 (61.26); H, 6.59 (6.50); N, 8.30 (8.40).

 $Cp*Ti{PhC(N^{i}Pr)_{2}}{N(C(Ar^{F_{5}})NO^{t}Bu)C(Ar^{F_{5}})NC(Ar^{F_{5}})N}$ (29). To a solution of Cp*Ti{PhC(NⁱPr)₂}(NO^tBu) (19; 0.250 g, 0.528 mmol) in benzene (5 mL) was added Ar^{Fs}CN (0.333 mL, 2.64 mmol), all at room temperature. A color change from dark green to lime green (26)to red was observed. After 6 h at room temperature, the volatiles were removed under reduced pressure, leaving behind an orange oil. Pentane (5 mL) was added and then removed under reduced pressure to afford 29 as an orange powder, which was dried in vacuo. Yield: 0.400 g (88%). An analytically pure sample was obtained by washing with pentane (5 mL) at room temperature, and the resultant orange powder was dried in vacuo. Yield: 0.222 g (49%). Diffraction-quality crystals were grown in the presence of $Ar^{F_5}CN$ from an Et₂O/pentane mixture at 4 °C. ¹H NMR (toluene- d_{8} , 499.9 MHz, 263 K): δ 7.45 (1 H, d, ${}^{3}J = 8.0$ Hz, o_{a} -C₆H₅), 7.20 (1 H, d, ${}^{3}J = 7.5$, o_{b} -C₆H₅), 7.12 (2 H, m, m-C₆H₅), 7.06 (1 H, m, p-C₆H₅), 3.83 (1 H, app sept, ³J = 6.5 Hz, NCH_aMeMe), 3.40 (1 H, app sept, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 2.27 $(15 \text{ H}, \text{ s}, \text{ C}_{5}\text{Me}_{5})$, 1.22 (9 H, s, OCMe₃), 1.06 (3 H, d, ³J = 7.0 Hz, NCH_aMeMe), 1.01 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_bMeMe), 0.80 (3 H, d, ${}^{3}J$ = 6.0 Hz, NCH_bMeMe), 0.73 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_aMeMe) ppm. ¹³C{¹H} NMR (toluene- d_{8} , 125.7 MHz, 263 K): δ 174.7 (PhCN₂), 155.7 (NCN), 148.2 (NCN), 146.9 (NCN), 129.4 (ob-C6H5), 129.1 $(p-C_6H_5)$, 128.8 ($o_a-C_6H_5$ overlapping with solvent), 127.6 ($m-C_6H_5$),

127.2 (C₅Me₅), 116.0 (1 C, m, *i*-C₆F₅), 114.2 (1 C, m, *i*-C₆F₅), 110.9 $(1 C, m, i-C_6F_5)$, 280.2 (OCMe₃), 51.5 (NCH_bMeMe), 46.2 (NCH_aMeMe), 27.3 (OCMe₃), 27.1 (NCH_aMeMe), 25.5 (CH_aMeMe), 24.5 (NCH_bMeMe) 13.0 (C₅Me₅) ppm. $^{13}C{^{19}F}$ NMR (toluene-d₈, 75.4 MHz, 263 K): 145.4 (o_{2b}-C₆F₅), 144.6 (overlapping o_3 -C₆F₅ and o_{1b} -C₆F₅), 144.3 (overlapping o_{1a} -C₆F₅ and o_{2a} -C₆F₅) 142.1 (p_1 -C₆F₅), 141.8 (p_2 -C₆F₅), 141.1 (p_3 -C₆F₅), 138.4 $(m_{1b}-C_6F_5)$, 137.8 $(m_3-C_6F_5)$, 137.7 $(m_{2a}-C_6F_5)$, 137.6 $(m_{2b}-C_6F_5)$, 137.1 $(m_{1a}-C_6F_5)$, ¹⁹F{¹H} NMR (toluene- d_8 , 470.4 MHz, 263 K): -126.7 (1 F, d, ${}^{3}J$ = 23.0 Hz, o_{1a} -C₆F₅), -134.16 (1 F, d, ${}^{3}J$ = 22.1 Hz, o_{1b} -C₆F₅), -137.0 (1F, d, ³J = 23.5 Hz, o_{2a} -C₆F₅), - 140.6 (1 F, app d, ${}^{3}J = 14.6$ Hz, o_{2b} -C₆F₅), -141.9 (2 F, m, o_{3} -C₆F₅), -150.9 (1 F, t, ${}^{3}J =$ 20.7 Hz, p_1 -C₆F₅), -154.0 (1 F, t, ${}^{3}J$ = 21.2 Hz, p_2 -C₆F₅), 155.5 (1 F, t, ${}^{3}J = 21.6, p_{3}-C_{6}F_{5}), -162.9 (2 \text{ F, m}, m_{3}-C_{6}F_{5}), -163.2 (2 \text{ F, t}, {}^{3}J = 22.1$ Hz, m_{1b} -C₆F₅), -163.9 (2 F, t, m, m_{2a} -C₆F₅), -164.1 (2 F, m, m_{2b} - C_6F_5), 165.0 (2 F, m, m_{1a} - C_6F_5) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1651 (w), 1595 (s), 1522 (s), 1491 (s), 1408 (s), 1366 (m), 1341 (w), 1316 (m), 1226 (w), 1215 (m), 1195 (m), 1147 (w), 1130 (m), 1117 (m), 1104 (w), 1078 (w), 1020 (w), 997 (s), 936 (m), 901 (w), 880 (w), 822 (m), 787 (w), 776 (w), 727 (w), 711 (w), 696 (w), 603 (w), 577 (w). Anal. Found (calcd for C₄₈H₄₃F₁₅N₆OTi): C, 54.88 (54.76); H, 4.17 (4.12); N, 7.82 (7.98).

Cp*Ti(O^tBu){NC(Ar^{F5})C(H)N(ⁱPr)C(Ph)N(ⁱPr)} (30). To a stirred solution of $Cp^*Ti{PhC(N^iPr)_2}(NO^tBu)$ (19; 0.298 g, 0.629 mmol) in Et₂O (5 mL) was added a solution of Ar^{F5}CCH (0.121 g, 0.629 mmol) in Et₂O (5 mL), all at room temperature. A color change from green to purple was observed. After 16 h, the volatiles were removed under reduced pressure and the resultant purple oily solid was extracted into cold pentane (2 \times 5 mL) and cooled to -78 °C. The volatiles were removed under reduced pressure to afford 30 as a purple powder, which was dried in vacuo. Yield: 0.290 g (69%). ¹H NMR (C₆D₆, 499.9 MHz, 293 K): δ 6.86 (3 H, m, overlapping o-C₆H₅ and NC(Ar^{F₅})C(H)N), 6.70 (2 H, t, ${}^{3}J = 7.0$ Hz, m-C₆H₅), 6.64 (1 H, m, $p-C_6H_5$), 3.91 (1 H, sept, ${}^{3}J = 6.5$ Hz, N(CH₂MeMe)C(H)), 3.61 (1 H, sept, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 2.09 (15 H, s, C₅Me₅), 1.37 (9 H, s, OCMe₃), 1.32 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH₄MeMe), 1.29 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_aMeMe), 1.27 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH_bMeMe), 0.77 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe) ppm. ${}^{13}C{}^{1}H$ NMR (C₆D₆, 125.7 MHz, 293 K): δ 161.6 (PhCN₂), 138.9 (NC(Ar^{F₅})C(H)N), 136.0 (*i*- C_6H_5), 128.5 (p- C_6H_5), 127.5 (m- C_6H_5), 127.4 (o- C_6H_5), 122.8 $(C_{5}Me_{5})$, 114.6 (1 C, t of d, ${}^{2}J_{C-F} = 15.1$ Hz, ${}^{3}J_{C-F} = 3.5$ Hz, $i-C_{6}F_{5})$, 108.8 (NC(Ar^{F₅})C(H)N), 82.2 (OCMe₃), 53.8 (NCH_aMeMe), 50.2 (NCH_bMeMe), 33.1 (OCMe₃), 27.0 (NCH_bMeMe), 26.7 (NCH_aMeMe), 24.9 (NCH_bMeMe), 24.6 (NCH_aMeMe), 12.3 (C_sMe_s) ppm. Note: ¹⁹F{¹H} NMR is broad at 293 K, and therefore ${}^{13}C{}^{19}F{}$ and ${}^{19}F{}^{1}H{}$ NMR spectra were recorded at 223 K. ${}^{13}C{}^{19}F{}$ NMR (toluene-d₈, 75.4 MHz, 223 K): 142.2 (o_a-C₆F₅), 141.2 (o_b- C_6F_5), 137.3 (m_b - C_6F_5), 137.0 (m_a - C_6F_5), 135.5 (p- C_6F_5) ¹⁹F{¹H} NMR (toluene- d_{8} , 282.1 MHz, 223 K): δ –142.6 (1 H, d, ³J = 21.7 Hz, $o_a - C_6 F_5$), -144.5 (1 H, d, ${}^3J = 24.8$ Hz, $o_b - C_6 F_5$), -165.7 (1 H, t, ${}^{3}J = 23.7$ Hz, m_{a} -C₆F₅), -166.2 (1 H, t, ${}^{3}J = 20.9$ Hz, m_{b} -C₆F₅), -167.6 (1 H, t, ${}^{3}J = 21.7$ Hz, $p-C_{6}F_{5}$) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1641 (w), 1603 (w), 1562 (w), 1544 (w), 1514 (s), 1484 (s), 1453 (s), 1342 (m), 1319 (w), 1260 (m), 1246 (m), 1211 (m), 1181 (m), 1092 (m), 1018 (m), 1002 (s), 980 (m), 910 (w), 803 (w), 748 (w), 715 (w), 702 (w). EI-MS: m/z 665 $[M]^+$ (65%). Anal. Found (calcd for C₃₅H₄₄F₅N₃OTi): C, 63.27 (63.16); H, 6.72 (6.66); N, 6.24 (6.31)

Cp*Ti{PhC(NⁱPr)₂}\eta^2-ON(H)B(Ar^{F₃})₃ (36). To a solution of Cp*Ti{PhC(NⁱPr)₂}(NOⁱBu) (19; 0.127 g, 0.269 mmol) in benzene (5 mL) was added a solution of B(Ar^{F₃})₃ (0.159 g, 0.538 mmol) in benzene (5 mL), and the mixture was heated to 70 °C. A color change from green to orange was observed. After 16 h the volatiles were removed under reduced pressure and the resulting orange solid washed with pentane (1 × 5 mL) at room temperature to afford 36 as an orange powder. Yield: 0.150 g (60%). An analytically pure sample was obtained from subsequent washing with benzene (2 × 5 mL) at room temperature and the orange powder dried in vacuo. Yield: 0.0671 mg (27%). Diffraction-quality crystals were grown from the

slow cooling of a saturated benzene solution. ¹H NMR (CD₂Cl₂, 499.9 MHz, 293 K): δ 7.51-7.41 (3 H, m, overlapping m-C₆H₅ and p-C₆H₅), 7.34 (1 H, m, o_a-C₆H₅), 7.19 (1 H, m, o_b-C₆H₅), 6.05 (1 H, s, NH), 3.61 (1 H, sept, ${}^{3}J = 6.5$ Hz, NCH₂MeMe), 3.22 (1 H, sept, ${}^{3}J =$ 6.5 Hz, NCH_bMeMe), 2.10 (15 H, s, C₅Me₅), 1.11 (3 H, d, ${}^{3}J$ = 6.5 Hz, NCH₂MeMe), 0.87 (3 H, d, ³J = 6.5 Hz, NCH₂MeMe), 0.74 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe), 0.60 (3 H, d, ${}^{3}J = 6.5$ Hz, NCH_bMeMe) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz, 293 K): δ 170.3 (PhCN₂), 148.7 (6 C, br d, ${}^{1}J_{C-F} = 237.1$ Hz, $o-C_{6}F_{5}$), 139.8 (3 C, br d, ${}^{1}J_{C-F} =$ 249.4 Hz, p-C₆F₅), 137.5 (6 C, br d, ${}^{1}J_{C-F}$ = 249.7 Hz, m-C₆F₅), 133.1 (i-C₆H₅), 130.0 (C₅Me₅), 129.7, 129.1, 129.0, 128.8 (o_a-C₆H₅, m-C₆H₅ and p-C₆H₅), 127.9 (o_b-C₆H₅), 121.1 (3 C, br s, i-C₆F₅), 51.1 (NCH₂MeMe), 50.3 (NCH_bMeMe), 26.8 (NCH₂MeMe), 26.2 (NCH_bMeMe), 24.0 (NCH_bMeMe), 23.6 (NCH_aMeMe), 12.5 (C_5Me_5) ppm. ¹¹B{¹H} NMR $(CD_2Cl_2, 96.2 \text{ MHz}, 298 \text{ K}): \delta -8$ $(B(C_6F_5)_3)$ ppm. Note: ¹⁹F{¹H} NMR is broad at 298 K and therefore was recorded at 253 K. ¹⁹F{¹H} NMR (CD₂Cl₂, 282.1 MHz, 253 K): δ -129.0 (1 F, br d., o_{1a} -C₆F₅), -130.5 (1 F, br d., o_{1b} -C₆F₅), -136.1 (2 F, br d., o_2 -C₆F₅), -145.5 (v br s, 2 F, o_3 -C₆F₅), -158.4 (1 F, br t, p_3 - C_6F_5), -158.7 (1 F, br t, p_1 - C_6F_5), -160.2 (1 F, br t, p_2 - C_6F_5), -161.6 (2 F, br t, m_3 -C₆F₅), -164.2 (1 F, br t, m_{1b} -C₆F₅), -165.2 (1 F, br t, m_{1a} -C₆F₅), -166.3 (2 F, br t, m_2 -C₆F₅) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3296 (w), 1644 (m), 1517 (s), 1338 (m), 1281 (m), 1220 (w), 1147 (w), 1092 (s), 1043 (w), 1021 (m), 980 (m), 958 (m), 811 (w), 782 (w), 732 (w), 723 (w), 708 (m), 695 (m), 676 (m). EI-MS: m/z 417 $[M-B(C_6F_5)_3]^+$, 512 $[B(C_6F_5)_3]^+$. Anal. Found (calcd for C₄₁H₃₅BF₁₅N₃OTi): C, 52.83 (52.99); H, 3.82 (3.80); N, 4.57 (4.52).

Computational Details. All the calculations have been performed with the Gaussian09 package at the B3PW91 level of hybrid density functional theory.⁶³ For the optimization of geometry, the titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis sets, augmented by an f polarization function.⁶⁴ The remaining atoms (C, H, N, O) were represented by a 6-31G(d,p) basis set. The solvent (toluene) influence was taken into consideration through single-point calculations on the gas-phase optimized geometry with the SMD model of PCM calculations.⁶⁵ For the PCM calculations the basis set on Ti was kept as in the gas-phase optimizations, but the remaining atoms were treated with a 6-311+G(d,p) basis set. All energies reported in Figure 6 are Gibbs free energies obtained by summing the PCM electronic energy, the gas-phase Gibbs contribution (T = 298, 253 K), and D3(bj) dispersion corrections.⁶⁶ The MO energies and the reaction energy in Figure 4 are from the gas-phase optimized geometry. NMR (GIAO) calculations of the magnetic shielding tensors of the oxime ethers (Figure S3 in the Supporting Information) were performed using an IGLOO-II basis set for the atoms.⁶⁷

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving general experimental procedures and details of starting materials, remaining details of the synthesis and characterization data for new compounds, X-ray data collection and processing parameters and X-ray crystallographic data for the structure determinations, and further details of the DFT calculations (Cartesian coordinates, pcm energy, NMR (GIAO) calculations of the magnetic shielding tensors of the oxime ethers **25a** and **25b**, Gibbs and dispersion corrections for the species in Figure 6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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